REMARKS

Applicants are pleased to note that claims 23 and 24 were allowed, and that claims 13 to 20, 32 to 39 and 44 to 49 were deemed to be allowable (see Item Nos. 4 and 5 on page 4 of the Office Action).

Claims 1 to 12, 21, 22, 25 to 31 and 38 to 43 were rejected under 35 USC 103 as being unpatentable over JP 2001-353814 (published December 25, 2001) for the reasons set forth in Item No. 1 on pages 2 to 3 of the Office Action.

Claim 26 was rejected under 35 USC 103 as being unpatentable over JP 2001-353814 and further in view of USP 5,585,177 to Okamura et al. for the reasons set forth in Item No. 1 on pages 3 to 4 of the Office Action.

Submitted herewith is an English-language translation of applicants' Japanese priority application 2001-360494 filed November 27, 2001, along with a STATEMENT OF ACCURACY OF TRANSLATION signed by Eiichi Ibaragi dated May 4, 2005.

Since applicants' JP 2001-360494 predates JP 2001-353814, withdrawal of JP 2001-353814 as a reference is respectfully requested.

In view of the above, withdrawal of the prior art rejections is respectfully solicited.

If the Examiner has any comments, questions, objections or recommendations, the Examiner is invited to telephone the undersigned at the telephone number given below for prompt action.

Respectfully submitted,

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Encs.: English-language translation of Japanese priority application 2001-360494 filed November 27, 2001 with STATEMENT OF ACCURACY OF TRANSLATION signed by Eiichi 9Ibaragi dated May 4, 2005.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

STATEMENT OF ACCURACY OF TRANSLATION
(37 C.F.R. 1.55 & 1.68)

The undersigned translator, having an office at

states that:

(1) I am fully conversant both with the Japanese and English languages.

(2)(A) I have translated into English Japanese Patent Application Number 2001-360494, filed November 27, 2001. A copy of said English translation is attached hereto.

(2)(B) I have carefully compared the attached English-language translation of Japanese Patent Application Number ________, filed ________ with the original Japanese-language patent application.

(3) The translation is, to the best of my knowledge and belief, an accurate translation from the original into the English language.

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[Designation of Document] SPECIFICATION

[Title of the Invention] RESIN FILM FOR METAL SHEET LAMINATE, RESIN LAMINATED METAL SHEET, AND METHOD FOR MANUFACTURING THE SAME

[Claims]

[Claim 1] A resin film for metal sheet laminate, comprising a mixed resin in which a granular resin mainly existing in a state of grains having 0.1 to 5 μm in diameter is dispersed in a polyester resin having a main basic skeleton of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate, in a range from 3 to 30% by weight in entire resin, the granular resin being a modified polyolefin resin containing a functional group derived from carboxylic acid in a range from 2 to 20% by weight as carboxylic acid.

[Claim 2] The resin film for metal sheet laminate as in claim 1, wherein the modified polyolefin resin in the film in a granular state from 0.1 to 5 μm in grain diameter is from 3 to 25% by volume in entire film.

[Claim 3] The resin film for metal sheet laminate as in claim 1 or claim 2, wherein the ratio of terephthalic acid to isophthalic acid, as a dicarboxylic acid component of the polyester resin, is from 97:3 to 85:15 by mole.

[Claim 4] The resin film for metal sheet laminate as in any of claims 1-3, wherein the resin film contains a pigment in a range from 5 to 40% by weight.

[Claim 5] A method for manufacturing resin film for metal sheet laminate according to any of claims 1-4, comprising the steps of: preparing a mixed resin as a raw material resin by preliminarily dispersing a granular modified polyolefin resin having grain diameters from 0.1 to 5 μm in a polyester resin having a main basic skeleton

of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate; and then charging the mixed resin to an extruding machine to melt the mixed resin to form the film.

[Claim 6] A laminated metal sheet comprising a metal sheet and a resin film coated on at least one side of the metal sheet, the resin film being manufactured by the method according to any of claims 1 to 4 or the method according to claim 5, having film thicknesses from 10 to 50 μm.

[Claim 7] The laminated metal sheet as in claim 6, wherein a plane orientation coefficient in the direction parallel to the film surface of the resin film is lower than 0.010.

[Claim 8] The laminated metal sheet as in claim 6 or claim 7, wherein the metal sheet is an electrolytic chromate treated steel sheet having a metallic chromium layer at coating weights from 50 to 200 mg/m^2 and a chromium oxide layer at coating weights from 3 to 30 mg/m^2 as metallic chromium, on the surface thereof.

[Claim 9] The laminated metal sheet as in any of claims 6-8, wherein the resin film coats a surface of the metal sheet by an extrusion laminating method.

[Claim 10] A method for manufacturing laminated metal sheet according to any of claims 6-8, comprising the step of laminating a resin film to a metal sheet which is heated to temperatures ranging from -70° C from the melting point of the polyester resin in the resin film to +30° C from the melting point thereof.

[Claim 11] A method for manufacturing laminated metal sheet according to claim 9, comprising the steps of: heating the mixed resin having the composition according to any of claims 1 to 4 to temperatures ranging from +10° C from the melting point of the polyester resin in the mixed resin to +40° C from the melting point thereof to melt the mixed resin; and then directly extruding the mixed resin onto a surface

of the metal sheet, thereby laminating the metal sheet.

[Claim 12] The method for manufacturing resin film for metal sheet laminate as in claim 11, comprising the steps of: preparing a mixed resin as a raw material resin by preliminarily dispersing a granular modified polyolefin resin having grain diameters from 0.1 to 5 μm in a polyester resin having a main basic skeleton of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate; charging the mixed resin to an extruding machine to melt the mixed resin; and then directly extruding the mixed resin onto a surface of the metal sheet, thereby laminating the metal sheet.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a resin film for metal sheet laminate, which resin film endures severe forming owing to excellent formability and impact resistance, and also owing to excellent adhesion to substrate metal even after forming and heating, and also to a laminated metal sheet, and a method for manufacturing the same.

[0002]

[Prior Art]

Conventionally, as a material for a metallic can that is subjected to severe forming, such as a thin-wall deep drawn can or a drawn and ironed can (DI can), a can provided with a resin layer on the internal surface thereof is generally used to prevent deteriorating in taste and flavor and further to prevent changes in properties of the contents due to dissolution of metal from the metal sheet. As such a can that is provided with a resin layer on the internal surface thereof and a resin-coated metal sheet capable of forming such a can, a metal sheet on which a polyester group resin is laminated

is used as a substitute resin film for epoxy group coating film of which danger of endocrine disrupter has recently been pointed.

[0003]

The polyester group resin used in such an application is required to provide the following performance: the adhesion to a metal sheet is excellent so that deformation such as elongation and compression of film caused by forming does not occur during the can manufacturing and deterioration of film and decrease in adhesion due to friction do not occur during the forming; the laminated polyester resin film is not crystallized or deteriorated after heat treatment such as drying, printing and pressing, and retorting after the can manufacturing, and separation and shrinkage of the film, cracks, pinholes, and other defects do not occur on the film; the polyester film is not cracked or separated by an impact to the can; corrosion or peeling does not occur when the polyester group resin comes into contact with various kinds of contents; flavor components of contents in the can are not adsorbed to the polyester film, or the flavor of the contents is not impaired by the dissolved components of polyester film and smell (hereinafter referred to as flavor property).

[0004]

For example, in Unexamined Japanese Patent Publication No. 59-232852, a metal sheet coated with polyethylene terephthalate group resin is proposed from a viewpoint of formability, heat resistance, corrosion resistance, flavor property, and the like. Also, in Unexamined Japanese Patent Publication No. 1-180336, a metal sheet coated with polybutylene terephthalate group resin is proposed. Furthermore, the coating resin used for that type of material for metallic can is requested to have excellent formability that withstands drawing and ironing, and also excellent adhesion such that a resin film does not separate from a steel sheet and impact resistance

such as to withstand shocks during can manufacturing, during canning, and during transportation. To meet the requirements, Unexamined Japanese Patent Publication Nos. 5-269920 and 6-320669 disclose a manufacturing method in which excellent formability, adhesion, and impact resistance can be obtained in addition to food sanitation property and flavor property, which a polyethylene terephthalate group resin film inherently has, by controlling the crystalline orientation of film by means of laminating technology or the like. Such a technology can be applied to the present requirement level for formability, adhesion, and impact resistance.

[0005]

However, in the concerned field, the decrease in sheet thickness is progressing year by year for decreasing the material weight, and this tendency is thought to continue in the future as well. In the above-described current manufacturing method for polyethylene terephthalate group resin, it is difficult to achieve both formability and impact resistance when the resin film is subjected to severer forming. The reason for this is that formability and impact resistance depend greatly on the crystalline orientation (plane orientation) of resin layer, and have a mutually contradictory tendency. Specifically, if a crystalline orientation component increases in the resin layer, plastic deformation is hindered by a crystalline portion, and hence formability is deteriorated. Therefore, from the viewpoint of formability, the smaller amount of oriented crystals is, the better formability is. However, since this crystalline portion acts as a portion for stopping the progress of crack under an impact, from the viewpoint of impact resistance, the larger amount of oriented crystals is, the higher impact resistance is. Thus, formability and impact resistance are designed by regulating the amount of oriented crystals so that both properties are in the allowable region. However, the

region in which both properties are compatible is the present limit of required performance so that it has been expected that a new highly formable film that can respond to an increase in the degree of forming in the future, and a laminated metal sheet coated with this film will be developed.

[0006]

In order to satisfy such a need, studies have been conducted earnestly on a technology in which both high formability and impact resistance are achieved by mixing a polyolefin resin with a polyester group resin. Unexamined Japanese Patent Publication No. 7-195617 discloses a technology in which a film structured by a composition of a saturated polyester resin and an ionomer resin is laminated to a metal sheet. Although the patent publication indicates that impact resistance can be kept even in an amorphous state, the impact resistance obtained merely by the addition of an ionomer is insufficient, and inversely, the orientation of polyester resin is actually hindered by the addition of an ionomer, which poses a problem in that the mechanical strength that polyester resin inherently has decreases, and resin is likely broken during forming.

[0007]

Furthermore, Unexamined Japanese Patent Publication No. 7-290643 discloses that impact resistance can be improved by laminating a ternary composition of polyester resin, polyester elastomer, and ionomer resin to a metal sheet. However, the mixture of this composition also has low capability for relaxing impact stress of polyester elastomer so that the effect of improving impact resistance of polyester resin is very little.

[0008]

On the other hand, WO 99/27026 Publication discloses a technology in which a rubber-like elastomer resin encapsulated by a

vinyl polymer having a polar group is finely dispersed in a polyester resin through blending the vinyl polymer having a polar group and the rubber-like elastomer resin into the polyester resin. Such fine dispersion of elastomer resin improves impact resistance so that the level of formability and impact resistance is high. However, the control of process for manufacturing such a capsule state is difficult to carry out, and the dispersed state of elastomer resin changes greatly depending on the resin-forming conditions, and is unstable. Therefore, there arises a problem in that the performance of the resultantly obtained resin film is not always constant. It is found that if such a dispersed state deviates from the optimum conditions, the performance decreases greatly. Even if a resin of such a composition is actually manufactured, a portion where the resin performance is low is produced partially so that the obtained performance such as formability and impact resistance is insufficient as a whole.

[0009]

[Problems that the Invention is to Solve]

Responding to the above problems, the present invention provides a means to solve the problems, which means provides a resin film for metal sheet laminate which endures severe forming owing to excellent formability and impact resistance, and also to excellent adhesion to substrate metal after forming and heating, further giving stable performance independent of forming conditions, and a method for manufacturing the same, also provides a laminated metal sheet, and a method for manufacturing the same.

[0010]

[Means for Solving the Problems]

The inventors carried out studies on the construction of resin layer that withstands further severe forming without losing advantage

of high formability that polyester resin (polyethylene terephthalate group resin) inherently has. Furthermore, the inventors pursued a resin composition by which that construction can be obtained stably regardless of the forming conditions. As a result, the inventors found that a resin having a structure in which a granular modified polyolefin resin having a specific composition is dispersed in a polyester resin provides drastically high formability and impact resistance, and also has excellent adhesion after forming and after heating. Moreover, since this resin construction can be obtained stably regardless of the forming conditions, stable performance is attained. Furthermore, it was verified that in this resin composition, necessary characteristics such as corrosion resistance and flavor property are also sufficient.

[0011]

The above resin composition can be obtained when a granular modified polyolefin resin containing a specific amount of a functional group derived from carboxylic acid is dispersed in the polyester resin. The modified polyolefin resin having such a functional group composition is dispersed in the polyester resin most stably, and moreover the mechanical properties of the modified polyolefin resin itself are optimal, thereby maximum formability and impact resistance can be provided.

[0012]

As the reason that both formability and impact resistance can be achieved, the following mechanism is presumed. When a destructive force acts on the resin by means of severe forming or impact, craze and crack are generated in the polyester resin, and the crack and craze grow, resulting in breakage. However, if the granular modified polyolefin resin having a proper composition and grain diameter is dispersed in the polyester resin, the progress of such craze and crack

is restrained by stress relaxation of the modified polyolefin resin, thus final occurrence of breakage can be prevented. Furthermore, there appears an effect that the plastic deformation of the polyester resin is accelerated in the sections were the modified polyolefin resin is in contact with the polyester resin, and hence stress concentration that results in breakage is relaxed, and the resin is less liable to be broken.

[0013]

The present invention has been made based on the above-described concept and findings, and the gist thereof is as described below.

(1) A resin film for metal sheet laminate, having a mixed resin in which a granular resin mainly existing in a state of grains having 0.1 to 5 μm in diameter is dispersed in a polyester resin having a main basic skeleton of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate, in a range from 3 to 30% by weight in entire resin, the granular resin being a modified polyolefin resin containing a functional group derived from carboxylic acid in a range from 2 to 20% by weight as carboxylic acid. (First aspect of the invention)

[0014]

(2) The resin film for metal sheet laminate as in (1), wherein the modified polyolefin resin in the film in a granular state from 0.1 to 5 μm in grain diameter is from 3 to 25% by volume in entire film. (Second aspect of the invention)

[0015]

(3) The resin film for metal sheet laminate as in (1) or (2), wherein the ratio of terephthalic acid to isophthalic acid, as a dicarboxylic acid component of the polyester resin, is from 97:3 to 85:15 by mole. (Third aspect of the invention)

[0016]

(4) The resin film for metal sheet laminate as in any of (1) to (3), wherein the resin film contains a pigment in a range from 5 to 40% by weight. (Fourth aspect of the invention)

[0017]

(5) A method for manufacturing resin film for metal sheet laminate according to any of (1) to (4), having the steps of: preparing a mixed resin as a raw material resin by preliminarily dispersing a granular modified polyolefin resin having grain diameters from 0.1 to 5 μm in a polyester resin having a main basic skeleton of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate; and then charging the mixed resin to an extruding machine to melt the mixed resin to form the film. (Fifth aspect of the invention)

[0018]

(6) A laminated metal sheet having a metal sheet and a resin film coated on at least one side of the metal sheet, the resin film being manufactured by the method according to any of (1) to (4) or the method according to (5), having film thicknesses from 10 to 50 μm. (Sixth aspect of the invention)

[0019]

(7) The laminated metal sheet as in (6), wherein a plane orientation coefficient in the direction parallel to the film surface of the resin film is lower than 0.010. (Seventh aspect of the invention)

[0020]

(8) The laminated metal sheet as in (6) or (7), wherein the metal sheet is an electrolytic chromate treated steel sheet having a metallic chromium layer at coating weights from 50 to 200 mg/m^2 and a chromium oxide layer at coating weights from 3 to 30 mg/m^2 as metallic

chromium, on the surface thereof. (Eighth aspect of the invention)

[0021]

(9) The laminated metal sheet as in any of (6) to (8), wherein the resin film coats a surface of the metal sheet by an extrusion laminating method. (Ninth aspect of the invention)

[0022]

(10) A method for manufacturing laminated metal sheet according to any of (6) to (8), having the step of laminating a resin film to a metal sheet which is heated to temperatures ranging from -70° C from the melting point of the polyester resin in the resin film to +30° C from the melting point thereof. (Tenth aspect of the invention)

[0023]

(11) A method for manufacturing laminated metal sheet according to (9), having the steps of: heating the mixed resin having the composition according to any of (1) to (4) to temperatures ranging from +10° C from the melting point of the polyester resin in the mixed resin to +40° C from the melting point thereof to melt the mixed resin; and then directly extruding the mixed resin onto a surface of the metal sheet, thereby laminating the metal sheet. (Eleventh aspect of the invention)

[0024]

(12) The method for manufacturing resin film for metal sheet laminate as in (11), having the steps of: preparing a mixed resin as a raw material resin by preliminarily dispersing a granular modified polyolefin resin having grain diameters from 0.1 to 5 μm in a polyester resin having a main basic skeleton of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate; charging the mixed resin to an extruding machine to melt the mixed resin; and then directly extruding the mixed resin onto a surface of

the metal sheet, thereby laminating the metal sheet. (Twelfth aspect of the invention)

[0025]

[Mode for Carrying Out the Invention]

Following is the description about the resin film for metal sheet laminate structured by a polyester resin containing the granular modified polyolefin resin according to the present invention dispersed therein, the laminated metal sheet, and the method for manufacturing the same.

According to the first aspect of the invention, the polyester resin having a main basic skeleton of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate means that the sum of the portion having sole structure unit of ethylene glycol and terephthalic acid in the skeleton of the polyester resin and/or the portion having structure units of ethylene glycol, terephthalic acid, and isophthalic acid therein occupies 90% by weight or more, while other portions allowing arbitrarily copolymerize with various kinds of aromatic dicarboxylic acid and aliphatic dicarboxylic acid. Specific examples of them are phthalic acid, 1,4-naphthalene dicarboxylic acid, 2,3-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, 4,4'-biphenyl dicarboxylic acid, diphenic acid, diphenyl ether carboxylic acid, 5-sulfoisophthalic acid, diphenoxy ethane dicarboxylic acid, adipic acid, oxalic acid, malonic acid, succinic acid, malic acid, citric acid, glutaric acid, dimer acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecadion acid, and trans-1,4-cyclohexane dicarboxylic acid.

[0026]

The glycol component may also copolymers of various kinds of aliphatic diol and aromatic diol. Examples of them are propylene

glycol, tetramethylene glycol, neopentyl glycol, pentamethylene glycol, hexamethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, trans-1,4-cyclohexanedimethanol, bisphenols, p-xylene glycol, cis-1,4-cyclohexanedimethanol, hydroquinone, 2,2-bis (4-β-hydroxyethoxyphenyl) propane, and hydrogenated bisphenol A.

[0027]

Furthermore, within the scope in which the object of the present invention is not impaired, a structure unit derived from a polyfunctional compound such as trimesic acid, pyromellitic acid, trimethylolethane, trimethylolpropane, trimethylolmethane, and pentaerythritol may be contained in a small amount, for example, 2% or less by weight.

[0028]

For the polyester resin in accordance with the present invention, the content of diethylene glycol is preferably 1.5% or lower by weight, and more preferably 0.9% or lower by weight. If the content of diethylene glycol in the polyester is high, deterioration of polymer progresses due to heat treatment such as drying and printing and pressing during forming, and hence cracks or pinholes are generated, thereby the impact resistance and flavor property are deteriorated in some cases.

[0029]

The intrinsic viscosity of polyester resin used in the present invention is preferably in a range from 0.3 to 2.0 dl/g, and more preferably from 0.5 to 1.0 dl/g. If the intrinsic viscosity is lower than 0.3 dl/g, mixing with modified polyolefin becomes significantly difficult to fail to attain uniform dispersion of the modified polyolefin resin, which may decrease mechanical strength and impact resistance. If the intrinsic viscosity exceeds 2.0 dl/g, the

formability becomes poor, which may fail to manufacture uniform film. The intrinsic viscosity is measured by the method specified in JIS K7367-5. It is measured in o-chlorophenol at 25℃ in a concentration of 0.005 g/ml, and is determined by the formula of [intrinsic viscosity $= (T - T_0) / (T_0 \times c)$]. In this formula, c expresses the resin concentration per 100 ml of solution in gram, and T_0 and T express drop time in a capillary viscometer of solvent and resin solution, respectively.

[0030]

Furthermore, the glass-transition temperature (Tg) of the polyester resin used in the present invention is preferably in a range from 50° C to 120℃, and more preferably from 60° C to 100℃. If the glass-transition temperature is lower than 50℃, a flaw and other defects are liable to be generated by a temperature rise during forming because of the deteriorated heat resistance of the polyester resin. On the other hand, if the glass-transition temperature exceeds 120℃, inversely the formability is deteriorated in some cases. Also, the low-temperature crystallization temperature (Tc) is usually in a range from 130° C to 210℃, preferably from 140° C to 200℃. The melting point (Tm) is usually in a range from 210° C to 265℃, preferably from 220° C to 260℃. If the low-temperature crystallization temperature is lower than 130℃, crystallization is liable to occur, thus the crystallization occurs during retorting, by which the film is easily cracked or separated. On the other hand, if the low-temperature crystallization temperature exceeds 210℃, the mechanical strength of polyester is deteriorated. If the melting point is lower than 210℃, the resin is deteriorated by the heat during forming, thereby cracks or pinholes are liable to be produced. On the other hand, if the melting point exceeds 265℃, the crystallization progresses due to the heat treatment such as drying and printing and pressing during

forming, and hence cracks or pinholes are also liable to be produced. The above-described glass-transition temperature, low-temperature crystallization temperature, and melting point are determined by measuring the endothermic peak temperature at the time of temperature rise using a differential scanning calorimeter (DSC). The measurement is made under conditions of a sample amount of 10 mg and a temperature rise rate of 10℃/min.

[0031]

The modified polyolefin resin having a functional group derived from carboxylic acid mixed in the polyester resin by 2 to 20% by weight as carboxylic acid, which is described in the first aspect of the invention, is required to be existing mainly in a fine granular state of 0.1 to 5 μm in terms of equivalent sphere diameter from the viewpoints of impact resistance, and of free from adverse effect on other characteristics such as formability and heat resistance. In this case, at least 30% by weight in the total modified polyolefin resin is required to be within a range from 0.1 to 5 μm in equivalent sphere diameter. Furthermore, the weight percentage of the modified polyolefin resin in the entire resin is required to be within a range from 3 to 30% by weight.

[0032]

If the modified polyolefin resin is dispersed in the polyester resin at the grain diameter range specified by the present invention, wide dispersion in grain diameter may occur from very fine grains not larger than 0.1 μm in diameter to coarse grains exceeding 5 μm. The grains smaller than 0.1 μm in diameter exert no influence on the physical properties of mixed resin. On the other hand, the grains exceeding 5 μm in diameter also do not improve the physical properties such as formability of mixed resin but rather decreases them. Therefore, at least 30% by weight of the whole modified polyolefin

resin must have diameters in a range from 0.1 to 5 μm in terms of equivalent sphere. From the viewpoint of restraining the decrease in physical properties, the ratio of grains exceeding 5 μm in diameter is preferably 1% or less by weight. Also, if the ratio of mixed modified polyolefin resin to the entire resin is lower than 3% by weight, the improvement in impact resistance is insufficient. If the ratio exceeds 30% by weight, performance such as formability and heat resistance is decreased.

[0033]

The glass-transition temperature of the modified polyolefin resin is preferably 0℃ or lower determined by the same measuring method as that for polyester resin. The temperature is more preferably -30℃ or lower. If the glass-transition temperature is above 0℃, the impact resistance becomes slightly poor, and is inferior especially at low temperatures.

Also, it is preferable that the Young's modulus is 100 MPa or lower and the breaking elongation is 200% or more at room temperature, and more preferable that the Young's modulus is 10 MPa or lower and the breaking elongation is 500% or more. The molecular weight is not subject to any special restriction, but it is preferably not lower than 2×10^3 and not higher than 1×10^6 in number-average molecular weight. If the molecular weight is lower than 2×10^3 or exceeds 1×10^6, the mechanical properties may be deteriorated and the impact resistance may be decreased, and additionally, forming may become difficult to do.

[0034]

The following is the description of a manufacturing method for the modified polyolefin resin. As a functional group derived from carboxylic acid, carboxylic acid group, carboxylic acid ester group, metal salt of carboxylic acid ion, and the like can be cited. The

modified olefin resin can be obtained by copolymerization, graft polymerization, or block polymerization of monomer containing these functional groups in polyolefin resin. As a monomer containing a functional group derived from carboxylic acid, concretely, acrylic acid, methacrylic acid, vinyl acetate, vinyl propionate, maleic acid, maleic anhydride, itaconic acid, unsaturated carboxylic acid with the number of carbons from 3 to 8 such as monomethylester maleate, and metal salt in which the whole or some of these acids is neutralized by metal cation of 1 or 2 valences such as sodium, potassium, lithium, zinc, magnesium, and calcium can be cited. The degree of neutralization is preferably 20 to 80%, and more preferably 30 to 70%. A composition formed from the modified polyolefin resin with such a degree of neutralization has a high melt extrusion property.

[0035]

Also, as carboxylate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-propyl acrylate, n-propyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-hydroxyethyl carboxylate, 2-hydroxyethyl methacrylate, monomethylester maleate, glycidyl acrylate, glycidyl methacrylate, vinyl acetate, acrylamine, acrylamide, and the like can be cited.

[0036]

The modified polyolefin resin containing a functional group derived from carboxylic acid can be obtained by copolymerization, block polymerization, or graft polymerization of a monomer containing a functional group derived from carboxylic acid with an olefin monomer containing no functional group derived from carboxylic acid, such as ethylene, propylene, 1-butane, 1-pentene, isobutene, isobutylene, butadiene, styrene, and acrylonitrile. Among these, in particular, the modified polyolefin resin obtained by graft polymerization or

copolymerization of carboxylic acid group in a polyolefin resin exhibits high performance. As such a modified polyolefin resin, commercially available resin is applicable, including Modiper A (manufactured by NOF Corp.), Nucrel (manufactured by Mitsui-DuPont Polychemical Co., Ltd.), Bondine (manufactured by Sumitomo Chemical Co., Ltd.), Admer (manufactured by Mitsui Chemicals, Inc.), and Tuftec (manufactured by Asahi Chemical Industry Co., Ltd.). Also, the modified polyolefin resin in which carboxylic acid is neutralized in apart by a metal salt can be used. For such a resin, though the formability is slightly low, the impact resistance is higher. As a commercially available resin, Himilan (manufactured by Mitsui-DuPont Polychemical Co., Ltd.) and the like can be cited. Furthermore, if zinc oxide, calcium hydroxide, or the like is added when a carboxylic acid modified polyolefin resin is melted and dispersed in the polyester resin, carboxyl group in the modified polyolefin resin is neutralized by metal ions thereof, and resultantly, a structure in which the carboxylic acid modified polyolefin resin in which the carboxylic acid is neutralized in a part by a metal salt is dispersed in polyester resin.

[0037]

The functional group derived from carboxylic acid is contained in amounts from 2 to 20%, preferably from 3 to 12% by weight in carboxylic acid. Within this composition range, the affinity with polyester resin and the dispersibility are enhanced to become maximum value. As the affinity of the modified polyolefin resin with the polyester resin as the matrix increases, the effect of relaxing interlayer fracture between different resins is enhanced at the moment of impact. As a result, the impact resistance is increased, and as the result that the cohesion of the modified polyester grains is restrained during forming, variations in performance due to forming

conditions are decreased. Such an effect can be obtained when the ratio of the functional group is 2% or higher by weight as carboxylic acid conversion. On the other hand, if the ratio exceeds 20% by weight, the affinity with the polyester resin decreases inversely, thereby the impact resistance is deteriorated.

[0038]

By dispersing the modified polyolefin resin in the polyester resin, the target mixed resin is obtained. As a method for dispersion, there is available, for example, a method in which two resins are melted and mixed together, and after the mixture is kept at a temperature at which one phase is formed, it is cooled to a temperature at which it is separated into two phases, by which the modified polyolefin resin phase is dispersed in the polyester resin phase by utilizing phase separation; a method in which after two resins are melted in a common solvent, the solvent is evaporated; a method in which the modified polyolefin resin in which the primary grain diameter has been made fine in advance to 1 μm or finer is melted and dispersed in the polyester resin at a temperature at which the resin does not cohere; a method in which the polyester resin is manufactured by polymerizing a monomer in a solution containing modified polyolefin resin in which the primary grain diameter has been made fine in advance to 1 μm or finer and a polyester resin forming monomer, and a state in which the modified polyolefin resin is dispersed in the polyester is established; or a method in which two resins are melted and mixed together, and the modified polyolefin resin is made fine by a mechanical shearing force. Any one of these methods is applicable.

[0039]

As an apparatus for mixing and melting, a mixing apparatus such as a tumbler blender, a Henschel mixer, and a V-type blender, or a melting/mixing apparatus such as an extruding machine of single screw

or twin screw, a kneader, and a Banbury type mixer can be used. With a combined use of these apparatuses, for example mechanical mixing by a tumbler blender followed by melting and mixing in an extruding machine, a highly dispersed mixed resin is obtained.

[0040]

Unless the effects of the present invention are hindered, an additive, such as a light stabilizer, impact resistance improving agent, compatibilizing agent, lubricant, plasticizer, antistatic agent, reaction catalyst, color preventing agent, free radical inhibitor, plasticizer, antistatic agent, terminal closing agent, oxidation inhibitor, heat stabilizer, mold releasing agent, flame retarder, antibacterial agent, and fungistat, may be added to the mixed resin. The content of these additives is preferably not lower than 0.005 parts by weight and not higher than 15 parts by weight, further preferably not lower than 0.01 parts by weight and not higher than 2 parts by weight, and most preferably not lower than 0.05 parts by weight and not higher than 0.5 parts by weight, with respect to 100 parts by weight of the mixed resin in the present invention. If the content is lower than 0.005 parts by weight, the effect is insufficient. On the other hand, if the content exceeds 15 parts by weight, the additive becomes excessive, thereby the mechanical properties of the mixed resin layer are decreased.

[0041]

As inorganic particles having the effect of improving lubricity, formability, impact resistance, silica manufactured by the dry method or wet method, porous silica, colloidal silica, titanium oxide, zirconium oxide, aluminum oxide, calcium carbonate, talc, calcium sulfate, barium sulfate, spinel, iron oxide, calcium phosphate, and the like can be cited. Also, as organic particles or polymeric organic particles, vinyl resin group particles such as polystyrene

particles, crosslinking polystyrene particles, styrene-acrylic group crosslinking particles, acrylic group crosslinking particles, styrene-methacrylate resin group crosslinking particles, and methacrylate resin group crosslinking particles, and particles containing the structural component of silicone, benzoguanamin-formaldehyde, polytetrafluoroethylene, polyphenolester, phenolic resin, and the like can be cited. The particle diameter and content of these particles are not subject to any special restriction. However, in order to achieve the performance to the utmost, the particle diameter is preferably in a range from 0.01 to 5 μm, and more preferably from 0.1 to 2.5 μm. Also, the particle diameter distribution is preferably sharp, and the standard deviation thereof is preferably 0.5 or less. As for the shape of particle, preferably the ratio of larger diameter to shorter diameter is from 1.0 to 1.2, and the particle is more preferably close to truly spherical.

[0042]

As a reaction catalyst, for example, an alkali metal compound, alkali earth metal compound, zinc compound, lead compound, manganese compound, cobalt compound, and aluminum compound can be cited, and as a color preventing agent, for example, a phosphorus compound can be cited.

[0043]

As a free radical inhibitor, one or more kinds selected from a phenol based free radical inhibitor, phosphorus based free radial inhibitor, sulfide based free radical inhibitor, and nitrogen based free radical inhibitor can be cited.

[0044]

As a plasticizer, a plasticizer structured by polyester obtained by terminal-esterifying a material obtained by condensation polymerization of an aliphatic polybasic acid with the number of

carbons of 2 to 20 or an aromatic polybasic acid with the number of carbons of 8 to 20 with respect to an ester derivative thereof or polybasic acid component with the molar ratio of the ester derivative of 0 to 2.0 with aliphatic alcohol with the number of carbons of 2 to 20 by monobasic acid with the number of carbons of 2 to 20 or its ester derivative and/or a monohydroxy alcohol with the number of carbons of 1 to 18 can be cited.

[0045]

As an antistatic agent, a method of kneading an antistatic agent disclosed in Unexamined Japanese Patent Publication No. 5-222357 in resin composition, a method of applying an antistatic agent disclosed in Unexamined Japanese Patent Publication No. 5-1164 on film surface, and the like method can be used as necessary in order to prevent electrostatic failure such as winding of film on a roll in the film forming process or contaminants adhering to film surface. As an antibacterial agent, a conventionally known antibacterial agent disclosed in Unexamined Japanese Patent Publication Nos. 11-48431 and 11-138702, and other literature can be used as necessary.

[0046]

The mixed resin according to the present invention preferably contains at least one element selected from germanium, antimony, and titanium from 1 to 500 ppm, and more preferably from 3 to 300 ppm. If the amount of element of at least one kind selected from germanium, antimony, and titanium is smaller than 1 ppm, the effect of improving flavor property is insufficient in some cases. If the amount exceeds 500 ppm, foreign matter is produced in the polyester and serves as a crystalline nucleus so that crystallization is liable to occur. In some cases, therefore, the impact resistance is deteriorated or heat resistance is decreased. Among these elements, germanium is especially favorable in terms of flavor property.

[0047]

A compound used for adding an element of at least one kind selected from germanium, antimony, and titanium to the polyester resin of the present invention are as follows. As a germanium compound, for example, germanium oxide such as germanium dioxide and crystallization water containing germanium hydroxide, hydroxide, or a germanium alkoxide compound such as germanium tetramethoxide, germanium tetraethoxide, germanium tetrabutoxide, and germanium ethyleneglycoxide, a germanium phenoxide compound such as germanium phenolate and germanium β-naphtholate, a phosphorus-containing germanium compound such as germanium phosphate and germanium phosphite, and germanium acetate can be cited.

[0048]

As an antimony compound, diantimony trioxide, antimony trifluoride, antimony acetate, antimony borate, antimony formate, antimonious acid, and the like can be cited.

[0049]

As a titanium compound, oxide such as titanium dioxide, hydroxide such as titanium hydroxide, an alcoxide compound such as tetramethoxy titanate, tetraethoxy titanate, tetrapropoxy titanate, tetraisopropoxy titanate, and tetrabutoxy titanate, a glycoside compound such as tetrahydroxyethyl titanate, a phenoxide compound, and a compound such as acetate can be cited.

[0050]

As a method for adding the above-described element to the polyester rein, arbitrary one of conventionally known methods can be used, and the method is not subject to any special restriction. It is preferable that the element be added as a polymerization catalyst usually at an arbitrary stage before the manufacture of polyester is finished. As such a method, in the case of germanium as an example,

a method in which a germanium compound powder is added as it is, a method in which a germanium compound is dissolved in a glycol compound, which is a starting material for polyester, and is added as described in Unexamined Japanese Patent Publication No. 54-22234, and the like method can be cited.

[0051]

Also, the content of acetaldehyde in the resin is preferably 10 ppm or lower, and more preferably 7 ppm or lower from the viewpoint of flavor property. If the content of acetaldehyde exceeds this range, especially over 10 ppm, the flavor property is deteriorated in some cases. The method for limiting the content of acetaldehyde to 10 ppm or lower is not subject to any special restriction. For example, a method can be cited in which the polyester resin is formed into a film, the polyester resin being obtained by a method in which resin is heat-treated at a temperature below the melting point of polyester under a reduced pressure or in an inert gas atmosphere to remove acetaldehyde generated by thermal decomposition when the polyester resin is manufactured by condensation polymerization or the like. A preferable method applies a polyester resin that is obtained by solid-phase polymerization at temperatures ranging from 150℃ or higher to the melting point thereof or lower under a reduced pressure or in an inert gas atmosphere. Also, the polyester resin in accordance with the present invention preferably has less oligomer structured by a cyclic trimer or the like from the viewpoint of flavor property. In particular, the content of cyclic trimer is preferably 0.9% or less by weight, and more preferably 0.7% or less by weight. If the content of the oligomer in resin exceeds this range, especially over 0.9% by weight, the flavor property is deteriorated in some cases. The method for limiting the content of oligomer to 0.9% or less by weight is not subject to any special restriction, and this content of oligomer can

be achieved using the same method as the above-described method for reducing the content of acetaldehyde.

[0052]

Regarding the mechanical properties of resin film structured by a mixed resin that withstand severe forming, the breakage elongation is preferably 20% or more, more preferably 50% or more, and the breakage strength is preferably 20 N/mm^2 or higher. Herein, the breakage elongation and breakage strength of resin film are determined using an ordinary tensile testing machine. As the tensile testing method, a resin coated layer measuring 5 mm x 60 mm is set at a distance of 30 mm between chucks, and the tensile test is conducted at a tensile speed of 20 mm/min at a constant temperature of 25℃. When tensile properties at low temperatures is determined, the same tensile test can be conducted at a constant temperature ranging from 0°C to -5℃. A resin sample for testing may be taken from any of film, resin laminated metal sheet, and formed body.

[0053]

According to the second aspect of the invention, it is specified that the amount of modified polyolefin resin existing in the film in granular state from 0.1 to 5 µm in grain diameter is in a range from 3 to 25% by volume in the entire film. As described above, the grains of smaller than 0.1 µm in diameter exert no influence on the physical properties of the mixed resin. On the other hand, the grains of larger than 5 µm in diameter also do not improve the physical properties such as formability of mixed resin but rather decreases them. Therefore, only the granular modified polyester resin from 0.1 to 5 µm in grain diameter in terms of equivalent sphere contributes to the improvement in impact resistance. Since the physical properties of film having grains of this diameter can be rearranged by the absolute value of volume in the whole film, the amount of modified polyolefin resin is

specified in a range from 3 to 25% by volume. If the volume ratio of modified polyolefin resin is lower than 3% by volume, the improvement in impact resistance is insufficient, and if it exceeds 25% by volume, the performance such as formability is decreased.

[0054]

Furthermore, the number of modified polyolefin resin grains existing in the mixed resin layer in granular state from 0.1 to 5 μm in diameter within a cube with 10 μm in each side (volume: 1000 μm^3) in the mixed resin is preferably from 5 to 10^5, and more preferably 50 to 10^4. If the number is smaller than 5, the improvement in impact resistance is insufficient, and if the number exceeds 10^5, the performance such as formability is decreased.

[0055]

According to the third aspect of the invention, the dicarboxylic acid component structuring the polyester resin in the mixed resin is specified that the ratio of total terephthalic acid to total isophthalic acid, as the dicarboxylic acid components of the polyester resin, is from 97:3 to 85:15 by mole. In the mixed resin in the present invention, the modified polyolefin in the resin hinders crystallization of the polyester resin, thus the decrease in adhesion and corrosion resistance caused by forming, heating, and the like is less liable to occur. Therefore, the optimum ratio extends toward the terephthalic acid rich side compared with the case where modified polyolefin resin is not contained. Thus, even if a homo-ethylene terephthalate resin that does not contain isophthalic acid at all is used as the polyester resin, when the polyester resin contains the modified polyolefin resin of the present invention, it can be used as an ordinary can material. Furthermore, if 3 % by mole of isophthalic acid is copolymerized, the adhesion after forming and heating increases drastically. If the amount of isophthalic acid increases

compared with the ratio of 85:15, the melting point is lowered and hence the heat resistance during forming may be deteriorated.

[0056]

According to the fourth aspect of the invention, it is specified that 5 to 40% by weight of a pigment is contained in the resin film because, in the polyester resin in which the modified polyolefin resin is dispersed, the dispersibility of pigment is improved, and the desired color tone can be obtained by the addition of a small amount of pigment. If the content of pigment is lower than 5% by weight, a desired color tone cannot be obtained, and if it exceeds 40% by weight, the formability is decreased. The kind of pigment is not subject to any special restriction. However, unless the effects of the present invention are hindered, calcium carbonate, barium sulfate, barium carbonate, aerosil, titanium dioxide, zinc white, gloss white, alumina white, magnesium carbonate, carbon black, magnetite, cobalt blue, iron oxide red, or the like is used appropriately, by which a metal laminated sheet or a metallic can can be finished so as to have a favorable color tone.

[0057]

According to the fifth aspect of the invention, a method for manufacturing resin film for metal sheet laminate according to any of the first to fourth aspects of the invention has the steps of: preparing a mixed resin as a raw material resin by preliminarily dispersing a granular modified polyolefin resin having grain diameters from 0.1 to 5 μm in a polyester resin having a main basic skeleton of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate; and then charging the mixed resin to an extruding machine to melt the mixed resin to form a film. With the method, a resin film having further uniform grain diameters of modified polyolefin resin is attained, thereby increasing the performance such

as impact resistance. Above-described method may be applied as the method to obtain the above mixed resin. In such a case, the temperature control such as temperature control and control of temperature changes is carried out more strictly than in the ordinary mixing method, the mixing time is prolonged, for example, about three to ten times compared with the ordinary mixing time, the mechanical shearing rate during mixing is increased, for example, about two to five times compared with the ordinary speed. By forming a film by charging such a mixed resin with high dispersibility and uniform grain diameters to an extruding machine and melting it, the grain diameter distribution of granular resin is narrowed remarkably compared with the case where the modified polyolefin resin is dispersed while a film is formed, and resultantly a film that achieves high grade in various performances can be obtained.

[0058]

According to the sixth aspect of the invention, the film thickness is restricted to a range from 10 to 50 μm in view of economy for the upper limit and of impact resistance and formability for the lower limit. If the film thickness becomes 10 μm or more, high impact resistance and formability are attained. If, however, the film thickness exceeds 50 μm, the resin film cost increases and the effect of increase in the impact resistance and the formability saturates.

[0059]

In the present invention, the metal sheet is not subject to any special restriction. However, a metal sheet formed of iron and aluminum is preferable in terms of formability. In the case of metal sheet formed of iron, in order to improve the resin adhesion and corrosion resistance, an inorganic oxide film layer, for example, a chemical conversion coating layer represented by chromic acid treatment, phosphoric acid treatment, chromic acid/phosphoric acid

treatment, electrolytic chromic acid treatment, chromate treatment, chromium-chromate treatment may be provided on the surface of metal sheet. Also, a malleable metal plating layer, for example, a plating layer of nickel, tin, zinc, aluminum, gun metal, brass may be provided. Also, the plating layer having the coating weights from 0.5 to 15 g/m^2 in the case of tin plating and 1.8 to 20 g/m^2 in the case of nickel or aluminum plating is especially preferable in terms of formability and resin adhesion. The thickness of such a metal sheet is usually 0.01 to 5 mm, preferably 0.1 to 2 mm. On one surface or both surfaces of the metal sheet, a resin laminated layer coated with the above-described resin composition layer in accordance with the present invention is formed.

[0060]

The reason why the plane orientation coefficient in the direction parallel with the film surface of resin film is specified to 0.010 or lower is that the resin film in this range especially has high formability. As the plane orientation coefficient increases, the formability becomes inferior. This is because oriented crystals hinder plastic deformation as described above. The range of plane orientation coefficient in accordance with the present invention is at a level at which adverse influence is not substantially exerted on the formability. Also, even in the range of plane orientation coefficient of the seventh aspect of the present invention, sufficiently high impact resistance is provided compared with the related art. However, considering the required formability and impact resistance, the plane orientation coefficient can also be increased intentionally to 0.010 or higher to obtain still higher impact resistance. The above-described film orientation can be obtained by laminating a stretched film to the metal sheet. Specifically, a film is stretched in the one-axis or two-axis direction

by a known method at the time of film manufacture to provide stretch orientation, and the stretched film is thermally laminated by being controlled so that the orientation remains at the laminating time, by which the film orientation can be obtained. Regarding the stretching of film, two-axis stretching is especially superior from the viewpoint of mechanical properties.

[0061]

In the case of metal sheet in which iron is used as the base material, the steel sheet subjected to electrolytic chromate treatment defined in the eighth aspect of the present invention is especially preferable in terms of adhesion to the resin film of the present invention, corrosion resistance, and manufacturing cost. Since the resin in accordance with the present invention has high adhesion after forming or heating, the optimum range of metallic chromium and chromium oxide is wider than that of the conventional resins. However, it has been found that when higher performance is demanded, the range of the present invention is the optimum one. The reason why the lower limit of the amount of metallic chromium in metallic chromium layer is specified to 50 mg/m^2 is that if the amount is smaller than 50 mg/m^2, the corrosion resistance and adhesion after forming are insufficient in some cases. The reason why the upper limit thereof is specified to 200 mg/m^2 is that if the amount exceeds 200 mg/m^2, the effect of improving the corrosion resistance and adhesion after forming is saturated, and inversely the manufacturing cost is increased. The reason why the lower limit of metallic chromium conversion amount of the amount of chromium in chromium oxide is specified to 3 mg/m^2 is that if the amount is smaller than 3 mg/m^2, the adhesion is deteriorated in some cases. The reason why the upper limit thereof is specified to 30 mg/m^2 is that if the amount exceeds 30 mg/m^2, the color tone is deteriorated, and also the adhesion becomes inferior.

[0062]

The reason why the resin film according to the ninth aspect of the invention is limited to the one that is coated by the extrusion laminating method is that the extrusion laminating method is superior to the ordinary film laminating method from the viewpoint of inclusion of air bubbles at the laminating time. In the general film laminating method, in particular, as the laminating speed increases, air bubbles are liable to be included. The included air bubbles not only decrease adhesion to a substrate metal sheet but also exert an adverse influence on impact resistance. The inventors found that since stresses concentrate in the edge portion of air bubble at the time of shock, this portion is brittle and serves as a starting point of film fracture. Furthermore, a difference in manufacturing cost between the process in which resin is formed into a film and laminated and the process in which resin is directly extruded and laminated is also an advantage of the extrusion laminating method. The resin in accordance with the present invention can be manufactured by the extrusion laminating method that cannot be used for the conventional polyester resin because the resin of the present invention can provide sufficient performance substantially even in a non-oriented state. The conventional polyester resin requires strict control of orientation amount so that it cannot be manufactured by direct extrusion that cannot be controlled strictly. As compared with this, the resin of the present invention also has a great advantage in terms of manufacture.

[0063]

According to the tenth aspect of the invention, the lower limit of the heating temperature of the metal sheet is specified to -70ºC from the melting point of the polyester resin in the mixed resin because the temperature below the lower limit gives insufficient adhesion to the metal sheet, and the upper limit thereof is specified to +30ºC

from the melting point of the polyester resin because the temperature above the upper limit induces fusion of the film layer onto the laminate roll. As described before, the resin of the present invention has excellent adhesion after forming and heating, thus the optimum range of manufacturing conditions for film laminate is wider than that of the conventional resins, thereby allowing labor saving and stabilizing in terms of manufacturing control and quality control, which is advantageous.

[0064]

According to the eleventh aspect of the invention, the melting temperature of the mixed resin is specified in a range from (Tm +10ºC) to (Tm +40ºC), (Tm designates the melting point of the polyester resin in the mixed resin). The reason of the specification is that the temperature lower than (Tm +10ºC) significantly reduces the viscosity of resin so that the quality stabilization and productivity become poor, and that the temperature above (Tm +40ºC) raises problems of adhesion to laminate roll, inclusion of air bubbles, deterioration of resin, and the like. Similarly, since the resin according to the present invention does not need strict control even in the manufacturing conditions for extrusion lamination, labor saving and stabilization in terms of manufacturing control and quality control are available, which is advantageous.

[0065]

According to the twelfth aspect of the invention, there is provided a method having the steps of: preparing a mixed resin as a raw material resin by preliminarily dispersing a granular modified polyolefin resin having grain diameters from 0.1 to 5 μm in a polyester resin having a main basic skeleton of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate; charging the mixed resin to an extruding machine to melt the mixed

resin; and then directly extruding the mixed resin onto a surface of the metal sheet, thereby laminating the metal sheet. Similar with the fifth aspect of the invention, the method provides a resin film with further uniform grain diameters of the modified polyolefin resin, thus improving the performance such as impact resistance.

With the method, there is provided a resin film with further uniform grain diameters of the modified polyolefin resin, thus improving the performance such as impact resistance. As a method to obtain the above mixed resin, the above mixing method can be applied. In that case, the temperature control such as temperature control and control of temperature changes is carried out more strictly than that of ordinary mixing method, the mixing time is prolonged, for example, about three to ten times compared with the ordinary mixing time, the mechanical shearing rate during mixing is increased, for example, about two to five times compared with the ordinary speed. By melting that resin having uniform grain diameters to form a film, the obtained grain diameter distribution of the granular resin becomes sharper than that of the method for dispersing the modified polyolefin while forming the film, thus allowing to attain superior performance in various characteristics.

[0066]

For the manufacturing of film, both a stretch oriented film and a non-stretched film can be used. Although a film is stretched in the one-axis or two-axis by a known method, the two-axis stretching is superior in view of mechanical performance. In the present invention, unless the effects of the present invention are hindered, a primer layer may be provided as an adhesion layer to metal sheet. Although the laminated metal sheet of the present invention has high primary adhesion between resin layer and metal sheet and high adhesion after forming, in a severer corrosive environment or in an environment

in which higher adhesion is required, a primer layer can be provided to provide characteristics that meet the requirement.

For example, when the laminated metal sheet is used as a metallic can, if more corrosive contents are put into the can, the contents intrude an interface with metal sheet through the resin layer, by which the metal sheet may be corroded, and the adhesion to film may be deteriorated. In such a case, a proper primer layer is provided to prevent the resin layer from being separated.

[0067]

The kind of primer is not subject to any special restriction, and a known primer layer can also be used. For example, a water-base dispersing agent of polyester resin group disclosed in Japanese Patent Publication No. 60-12233, an epoxy based primer disclosed in Japanese Patent Publication No. 63-13829, and a polymer having various functional groups disclosed in Unexamined Japanese Patent Publication No. 61-149341 can be cited. Also, a method for forming a primer layer is not subject to any special restriction. A primer paint may be applied on the metal sheet and dried, or a primer paint may be applied on the film of the present invention and dried. Alternatively, a primer film may be laminated to the metal sheet, or a film formed by affixing a primer layer to the film of the present invention may be laminated.

[0068]

The resin laminated metal sheet according to the present invention is only requested to be coated by a resin film according to the present invention, and at need, a known resin film may be laminated as the lower layer and/or upper layer of the resin film of the present invention to cover the metal sheet.

[0069]

The resin film for metal sheet laminate is suitably used for

inner coating of two-piece metallic can manufactured by drawing or ironing. The film according to the present invention has favorable metal adhesion and formability as coating for a lid of two-piece can and for a sidewall, a lid, and a bottom of three-piece can so that the film is also favorably used in that use.

[0070]

Since the laminated metal sheet coated by the film has excellent formability, impact resistance, and adhesion, it is suitable as a material for a thin-wall deep drawn can which is subjected to particularly severe forming in a current state of thinning the can wall thickness by reducing sheet thickness of the material.

[0071]

[Examples]

<Example 1>

A modified polyolefin resin with a group derived from carboxylic acid having a primary grain diameter of 0.3 μm, which was a starting raw material, was cold-blended with a polyester resin in a blending ratio given in Tables 1 and 2 using a tumbler blender, and then the blended resin was melted and kneaded at 260℃ using a twin screw extruding machine, by which a raw material pellet of polyester resin in which the modified polyolefin resin was dispersed was obtained. The obtained raw material resin pellet was extruded from a T-die using a single screw extruding machine, by which a resin film with a thickness in arrange from 5 to 55 μm was manufactured.

[0072]

The used polyester resin and the modified polyolefin resin with a group derived from carboxylic acid were as follows.

[0073]

1. Polyester resin

(1) PET/I(18): An ethylenephthalate-ethyleneisophthalate

copolymerized resin with a ratio of terephthalic acid to isophthalic acid of 82:18 (manufactured by Kanebo Gohsen, Ltd.), intrinsic viscosity: 0.6 dl/g, Tg: 58℃, Tc: 210℃, Tm: 215℃, Ge content: 10 ppm

(2) PET/I(10): An ethylenephthalate-ethyleneisophthalate copolymerized resin with a ratio of terephthalic acid to isophthalic acid of 90:10 (IP121B manufactured by Kanebo Gohsen, Ltd.), intrinsic viscosity: 0.6 dl/g, Tg: 70℃, Tc: 170℃, Tm: 230℃, Ge content: 10 ppm

(3) PET/I(5): An ethylenephthalate-ethyleneisophthalate copolymerized resin with a ratio of terephthalic acid to isophthalic acid of 95:5 (manufactured by Kanebo Gohsen, Ltd.), intrinsic viscosity: 0.62 dl/g, Tg: 72℃, Tc: 156℃, Tm: 255℃, Ge content: 20 ppm

(4) PET/I(2): An ethylenephthalate-ethyleneisophthalate copolymerized resin with a ratio of terephthalic acid to isophthalic acid of 98:2 (manufactured by Kanebo Gohsen, Ltd.), intrinsic viscosity: 0.6 dl/g, Tg: 68℃, Tc: 150℃, Tm: 250℃, Ge content: 10 ppm

(5) PET: A homopolyethylene phthalate resin (EFG10 manufactured by Kanebo Gohsen, Ltd.), intrinsic viscosity: 0.62 dl/g, Tg: 72℃, Tc: 150℃, Tm: 255℃, Ge content: 20 ppm

[0074]

2. Modified polyolefin resin with a group derived from carboxylic acid

(1) EM1: A polymethyl methacrylate-(ethylene-ethyl acrylate copolymer) graft copolymer (Modiper A5200 manufactured by NOF Corp.), weight ratio of functional group derived from carboxylic acid: 21 wt%, glass-transition temperature: -30℃ or lower

(2) EM2: A polymethyl methacrylate-(ethylene-ethyl acrylate-maleic anhydride copolymer) graft copolymer (Modiper A8200

manufactured by NOF Corp.), weight ratio of functional group derived from carboxylic acid: 18 wt%, glass-transition temperature: -30℃ or lower

(3) EM3: An ethylene-ethyl acrylate-maleic anhydride copolymer (Bondine HX8290 manufactured by Sumitomo Chemical Co., Ltd.), weight ratio of functional group derived from carboxylic acid: 11 wt%, glass-transition temperature: -30℃ or lower

(4) EM4: An ethylene-methacrylic acid copolymer (Nucrel N1560 manufactured by Mitsui-DuPont Polychemical Co., Ltd.), weight ratio of functional group derived from carboxylic acid: 8 wt%, glass-transition temperature: -30℃ or lower

(5) EM5: A 50% Zn neutralized substance of ethylene-methacrylic acid copolymer (Nucrel N1560 manufactured by Mitsui-DuPont Polychemical Co., Ltd. neutralized partially by Zn), weight ratio of functional group derived from carboxylic acid: 7 wt%, glass-transition temperature: -30℃ or lower

(6) EM6: A 70% Zn neutralized substance of ethylene-methacrylic acid copolymer (Nucrel N1035 manufactured by Mitsui-DuPont Polychemical Co., Ltd. neutralized partially by Zn), weight ratio of functional group derived from carboxylic acid: 5 wt%, glass-transition temperature: -30℃ or lower

(7) EM7: An ethylene-methacrylic acid copolymer (Nucrel N0200H manufactured by Mitsui-DuPont Polychemical Co., Ltd.), weight ratio of functional group derived from carboxylic acid: 1 wt%, glass-transition temperature: -30℃ or lower

(8) EM8: A polystyrene-(ethylene-ethyl acrylate copolymer) graft copolymer (Modiper A5100 manufactured by NOF Corp.), weight ratio of functional group derived from carboxylic acid: 6 wt%, glass-transition temperature: 20℃

(9) EPR: An ethylene-propylene rubber (EP07P manufactured by

JSR Corp.), weight ratio of functional group derived from carboxylic acid: 0 wt%, glass-transition temperature: -30℃ or lower

[0075]

A pelletized modified polyolefin resin with a group derived from carboxylic acid, which was a starting raw material, was mixed with a polyester resin in a blending ratio given in Comparative example 14 in Table 1, the mixed resin was melted and kneaded at 260℃ using a single screw extruding machine, and the mixed resin of the modified polyolefin resin and the polyester resin was extruded from a T-die, by which a resin film with a thickness of 25 μm was manufactured.

[0076]

For the grain diameter of modified polyolefin resin dispersed in resin film, the polyester resin in the surface layer was etched by an alkaline aqueous solution and the modified polyolefin grains were caused to remain, the larger diameter and shorter diameter thereof were measured one by one, and the grain diameter (in terms of equivalent sphere) was calculated, by which the volume ratio, i.e., the number of grains in the film with one side of 10 μm was determined. Also, various temperatures in the tables were measured by a method using the aforementioned DSC.

[0077]

As a metal sheet, a tin-free steel (hereinafter abbreviated to TFS) with a thickness of 0.18 mm for thin-wall deep drawn can and 0.23 mm for DI can, which had a degree of temper of DR9, metallic chromium layer of 80 mg/m^2, and chromium oxide layer of 15 mg/m^2 (as metallic chromium), was used, by which a laminated metal sheet was obtained by a thermo-compression bonding method in which the resin film obtained as described above was hot-pressed on both surfaces of the metal sheet heated by an induction heating system, and then the laminated metal sheet was rapidly cooled in water. The metal sheet

temperature during laminating (laminating temperature) is given in Tables 3 and 4.

[0078]

For the plane orientation coefficient of resin laminated metal sheet, the refractive index was measured using Abbe's refractometer. In measuring, the light source was a sodium/D ray, the intermediate solution was methylene iodide, and the temperature was 25℃. Then, the refractive index Nx in the lengthwise direction of metal sheet on the film surface, the refractive index Ny in the widthwise direction of metal sheet on the film surface, and the refractive index Nz in the film thickness direction were determined, and the plane orientation coefficient Ns was calculated by the following equation.

Plane orientation coefficient (Ns) = (Nx+Ny)/2 - Nz

[0079]

Furthermore, the resin laminated metal sheet obtained as described above was formed into a can, and subjected to straightening heat treatment to manufacture a sample can. The formability, impact resistance, adhesion after forming, and adhesion after heating of film of manufactured can body were investigated.

[0080]

The following is the detailed description of the investigation method.

1. Evaluation by thickness-decreasing deep drawing

For a resin laminated metal sheet using a TFS with a thickness of 0.18 mm, a thin-wall deep drawn can was manufactured by the method described below, and the propriety of thin-wall deep drawn can was investigated.

1-1. Can manufacturing

A resin laminated metal sheet was subjected to first-stage

drawing and redrawing under the following conditions, by which a thin-wall deep drawn can was obtained.

・First-stage drawing

Blank diameter … 150 to 160 mm

First-stage drawing … drawing ratio: 1.65

・Redrawing

Primary redrawing … drawing ratio: 1.25

Secondary redrawing … drawing ratio: 1.25

Radius of curvature of die corner in redrawing process … 0.4 mm

Load for pressing wrinkle at the time of redrawing … 39227N (4000 kg)

・Average thickness decreasing percentage of can sidewall

40 to 55% with respect to thickness of resin laminated metal sheet before forming

1-2. Straightening heat treatment

Forming strain of film caused by can manufacturing was removed by keeping the can in a thermal environment of film melting point minus 15℃ for 30 seconds and then by rapidly cooling it.

[0081]

1-3. Evaluation of propriety of thin-wall deep drawn can

(1) Formability

Evaluation was made as described below by the limit of capability for manufacturing can without film failure. Grades not lower than ○ marked grade are acceptable.

Limit of forming (thickness decreasing percentage) : Grade

Incapable of forming at thickness decreasing percentage of 40%: ××(Inferior)

Capable of forming up to thickness decreasing percentage of 40%: ×

↑

Capable of forming up to thickness decreasing percentage of 45%: □
Capable of forming up to thickness decreasing percentage of 50%: ○
↓
Capable of forming up to thickness decreasing percentage of 55%: ◎
(Superior)

[0082]

(2) Evaluation of room-temperature and low-temperature impact resistance

A can body (thickness decreasing percentage: 50%) subjected to straightening heat treatment was necked, and the can body was filled with distilled water. After a lid was installed and tightened, an iron ball of 0.5 kg was dropped from a height of 30 cm to give a shock to the can bottom. Thereafter, the lid was opened, and 1% salt water was poured in the can so that a portion that had suffered shock was immersed. After immersion for five minutes, a load of 6 V was applied across a platinum electrode immersed in the liquid and a can metal portion, and the current value after five minutes was read, by which evaluation was made as described below. The same tests were conducted at room temperature of 20℃ and at a temperature of 0℃. The former test was for evaluating room-temperature impact resistance, and the latter test was for evaluating low-temperature impact resistance. Grades not lower than ○ marked grade are acceptable.

(Evaluation of room-temperature impact resistance)
Test result : Grade
Current value not lower than 30 mA: XX (Inferior)
Current value not lower than 10 mA and lower than 30 mA: × ↑
Current value not lower than 5 mA and lower than 10 mA: □
Current value not lower than 1 mA and lower than 5 mA: ○ ↓
Current value lower than 1 mA : ◎ (Superior)

(Evaluation of low-temperature impact resistance)

Test result : Grade

Current value not lower than 30 mA: △ (Inferior)

Current value not lower than 10 mA and lower than 30 mA: ○ ↑

Current value not lower than 5 mA and lower than 10 mA: ◎

Current value not lower than 1 mA and lower than 5 mA: ◎◎ ↓

Current value lower than 1 mA : ◎◎◎ (Superior)

[0083]

(3) Adhesion after forming

The internal surface of can body subjected to straightening heat treatment was cleaned, and the can was immersed in an aqueous solution containing 1.5 wt% citric acid and 1.5 wt% sodium chloride for 24 hours. Thereafter, the peeling length of resin in the can end portion was observed, and evaluation was made as described below. Grades not lower than ○ marked grade are acceptable.

Test result : Grade

Peeling length longer than 10 mm : ×× (Inferior)

Peeling length longer than 5 mm and not longer than 10 mm: × ↑

Peeling length longer than 2 mm and not longer than 5 mm: △

Peeling length not longer than 2 mm: ○ ↓

No peeling : ◎ (Superior)

[0084]

(4) Adhesion after heating

The internal surface of can body subjected to straightening heat treatment was cleaned, and the can was heated without content therein at 210℃ for 10 minutes in an oven. Thereafter, the degree of peeling of resin in the can end portion was observed, and evaluation

was made as described below. Grades not lower than ○ marked grade are acceptable.

Test result : Grade

Peeling percentage higher than 10% : ×× (Inferior)

Peeling percentage higher than 5% and not higher than 10%: × ↑

Peeling percentage higher than 2% and not higher than 5%: △

Peeling percentage not higher than 2%: ○ ↓

No peeling : ◎◎ (Superior)

[0085]

2. Evaluation by drawing and ironing (DI forming)

For a resin laminated metal sheet using a TFS with a thickness of 0.23 mm, a DI can was manufactured by the method described below, and the propriety of DI can was investigated.

[0086]

2-1. Can manufacturing

A resin laminated metal sheet was drawn and ironed under the following conditions, by which a DI can was obtained.

・First-stage drawing

Blank diameter: 150 mm

Drawing ratio: 1.6

・Second-stage drawing

Drawing ratio: 1.25

・Ironing

Ironing punch diameter: 3-stage ironing 65.8 mm dia

・Total ironing percentage of can sidewall

55 to 70% with respect to thickness of resin laminated metal sheet before forming

[0087]

2-2. Straightening heat treatment

Forming strain of film caused by can manufacturing was removed by keeping the can in a thermal environment of film melting point minus 15℃ for 30 seconds and then by rapidly cooling it.

[0088]

2-3. Evaluation of propriety of DI can

(1) Formability

Evaluation was made as described below by the limit of capability for manufacturing can without film failure. Grades not lower than ○ marked grade are acceptable.

Limit of forming (total ironing percentage) : Grade

Incapable of forming at total ironing percentage of 55%: ×× (Inferior)

Capable of forming up to total ironing percentage of 55%: × ↑

Capable of forming up to total ironing percentage of 60%: △

Capable of forming up to total ironing percentage of 65%: ○ ↓

Capable of forming up to total ironing percentage of 70%: ◎ (Superior)

[0089]

(2) Evaluation of room-temperature and low-temperature impact resistance

A can body (total ironing percentage: 65%) subjected to straightening heat treatment was necked, and the can body was filled with distilled water. After a lid was installed and tightened, an iron ball of 0.5 kg was dropped from a height of 25 cm to give a shock to the can bottom. Thereafter, the lid was opened, and 1% salt water was poured in the can so that a portion that had suffered shock was immersed. After immersion for five minutes, a load of 6 V was applied across a platinum electrode immersed in the liquid and a can metal portion, and the current value after five minutes was read, by which

evaluation was made as described below. The same tests were conducted at room temperature of 20℃ and at a temperature of 0℃. The former test was for evaluating room-temperature impact resistance, and the latter test was for evaluating low-temperature impact resistance. Grades not lower than ○ marked grade are acceptable.

(Evaluation of room-temperature impact resistance)

Test result : Grade

Current value not lower than 30 mA: ×× (Inferior)

Current value not lower than 10 mA and lower than 30 mA: × ↑

Current value not lower than 5 mA and lower than 10 mA: △

Current value not lower than 1 mA and lower than 5 mA: ○ ↓

Current value lower than 1 mA : ◎ (Superior)

(Evaluation of low-temperature impact resistance)

Test result : Grade

Current value not lower than 30 mA: △ (Inferior)

Current value not lower than 10 mA and lower than 30 mA: ○ ↑

Current value not lower than 5 mA and lower than 10 mA: ◎

Current value not lower than 1 mA and lower than 5 mA: ◎◎ ↓

Current value lower than 1 mA : ◎◎◎ (Superior)

[0090]

(3) Adhesion after forming

The internal surface of can body subjected to straightening heat treatment was cleaned, and the can was immersed in an aqueous solution containing 1.5 wt% citric acid and 1.5 wt% sodium chloride for five hours. Thereafter, the peeling length of resin in the can end portion was observed, and evaluation was made as described below. Grades not lower than ○ marked grade are acceptable.

Test result : Grade

Peeling length longer than 10 mm : ×× (Inferior)

Peeling length longer than 5 mm and not longer than 10 mm:

× ↑

Peeling length longer than 2 mm and not longer than 5 mm: △

Peeling length not longer than 2 mm: ○ ↓

No peeling : ◎ (Superior)

[0091]

(4) Adhesion after heating

The internal surface of can body subjected to straightening heat treatment was cleaned, and the can was heated without contents therein at 210℃ for 10 minutes in an oven. Thereafter, the degree of peeling of resin in the can end portion was observed, and evaluation was made as described below. Grades not lower than ○ marked grade are acceptable.

Test result : Grade

Peeling percentage higher than 10% : ×× (Inferior)

Peeling percentage higher than 5% and not higher than 10%: × ↑

Peeling percentage higher than 2% and not higher than 5%: △

Peeling percentage not higher than 2%: ○ ↓

No peeling : ◎ (Superior)

The investigation results are given in Tables 3 and 4.

[0092]

[Table 1]

Sample film	Film thickness (μm)	Polyester resin		Pigment		Polyolefin resin						Stretching
		Resin type	Additive	Kind	Content *1)	Resin type	Weight percentage of functional group derived from carboxylic acid (wt%)	Tg (℃)	Blending ratio in entire resin (wt%)	Volume percentage of grains with diameter of 0.1 to 5 μm (vol%)	Number of grains with diameter of 0.1 to 5 μm in cube with one side of 10 μm (grains)	
Invention example 1	25	PET/I(18)	None	None	0	EM4	8	<-30	15	12	2000	Non-stretched
Invention example 2	25	PET/I(10)	None	None	0	EM4	8	<-30	15	12	2000	Non-stretched
Invention example 3	25	PET/I(5)	None	None	0	EM4	8	<-30	15	12	2000	Non-stretched
Invention example 4	25	PET/I(2)	None	None	0	EM4	8	<-30	15	12	2000	Non-stretched
Invention example 5	25	PET	None	None	0	EM4	8	<-30	15	12	2000	Non-stretched
Invention example 6	25	PET/I(10)	None	None	0	EM2	18	<-30	15	13	500	Non-stretched
Invention example 7	25	PET/I(10)	None	None	0	EM4	8	<-30	15	12	2000	Non-stretched
Invention example 8	25	PET/I(10)	None	None	0	EM5	7	<-30	15	12	2000	Non-stretched
Invention example 9	25	PET/I(10)	None	None	0	EM6	5	<-30	15	12	2000	Non-stretched
Invention example 10	25	PET/I(10)	None	None	0	EM8	6	20	15	12	2000	Non-stretched
Invention example 11	25	PET/I(10)	None	None	0	EM3	11	<-30	5	3	3	Non-stretched
Invention example 12	25	PET/I(10)	None	None	0	EM3	11	<-30	5	5	70	Non-stretched
Invention example 13	25	PET/I(10)	None	None	0	EM3	11	<-30	10	8	30	Non-stretched
Invention example 14	25	PET/I(10)	None	None	0	EM3	11	<-30	10	10	250	Non-stretched
Invention example 15	25	PET/I(10)	None	None	0	EM3	11	<-30	15	15	500	Non-stretched
Invention example 16	25	PET/I(10)	None	None	0	EM3	11	<-30	15	18	20000	Non-stretched
Invention example 17	25	PET/I(10)	None	None	0	EM3	11	<-30	20	22	200000	Non-stretched
Invention example 18	25	PET/I(10)	None	None	0	EM3	11	<-30	25	20	8000	Non-stretched
Invention example 19	25	PET/I(10)	None	TiO_2	3	EM5	7	<-30	15	12	2000	Non-stretched
Invention example 20	25	PET/I(10)	None	TiO_2	7	EM5	7	<-30	15	12	2000	Non-stretched
Invention example 21	25	PET/I(10)	None	TiO_2	15	EM5	7	<-30	15	12	2000	Non-stretched
Invention example 22	25	PET/I(10)	None	TiO_2	30	EM5	7	<-30	15	12	2000	Non-stretched
Invention example 23	25	PET/I(10)	None	TiO_2	50	EM5	7	<-30	15	12	2000	Non-stretched
Invention example 24	5	PET/I(10)	None	None	0	EM6	5	<-30	15	12	2000	Non-stretched

*1) Pigment content means weight percentage (wt%) of pigment with respect to total film amount of entire resin and pigment.

[0093]

[Table 2]

Sample film	Film thickness (μm)	Polyester resin		Pigment		Polyolefin resin						Stretching
		Resin type	Additive	Kind	Content *1)	Resin type	Weight percentage of functional group derived from carboxylic acid (wt%)	Tg (℃)	Blending ratio in entire resin (wt%)	Volume percentage of grains with diameter of 0.1 to 5 μm 0.2 (vol%)	Number of grains with diameter of 0.1 to 5 μm in cube with one side of 10 μm (grains)	
Invention example 25	15	PET/I(10)	None	None	0	EM6	5	<-30	15	12	2000	Non-stretched
Invention example 26	20	PET/I(10)	None	None	0	EM6	5	<-30	15	12	2000	Non-stretched
Invention example 27	40	PET/I(10)	None	None	0	EM6	5	<-30	15	12	2000	Non-stretched
Invention example 28	55	PET/I(10)	*2)0.3wt%	None	0	EM6	5	<-30	15	12	2000	Non-stretched
Invention example 29	25	PET/I(10)	*3)0.1wt%	None	0	EM3	11	<-30	15	12	2000	Non-stretched
Invention example 30	25	PET/I(10)	*4)3wt%	None	0	EM3	11	<-30	15	13	2000	Non-stretched
Invention example 31	25	PET/I(10)	None	None	0	EM3	11	<-30	15	12	2000	Non-stretched
Invention example 32	25	PET/I(10)	None	None	0	EM4	8	<-30	15	12	2000	Two-axis stretched
Invention example 33	25	PET70%+ PET/I(10)30%	None	None	0	EM4	8	<-30	15	12	2000	Non-stretched
Invention example 34	25	PET40%+ PET/I(18)60%	None	None	0	EM4	8	<-30	15	12	2000	Non-stretched
Comparative example 1	25	PET/I(18)	None	None	0	None	-	-	0	0	0	Non-stretched
Comparative example 2	25	PET/I(10)	None	None	0	None	-	-	0	0	0	Non-stretched
Comparative example 3	25	PET/I(10)	None	None	0	None	-	-	0	0	0	Two-axis stretched
Comparative example 4	25	PET/I(5)	None	None	0	None	-	-	0	0	0	Non-stretched
Comparative example 5	25	PET/I(2)	None	None	0	None	-	-	0	0	0	Non-stretched
Comparative example 6	25	PET	None	None	0	None	-	-	0	0	0	Non-stretched
Comparative example 7	25	PET/I(10)	None	None	0	EM3	11	<-30	2	2	3	Non-stretched
Comparative example 8	25	PET/I(10)	None	None	0	EM3	11	<-30	2	2	45	Non-stretched
Comparative example 9	25	PET/I(10)	None	None	0	EM3	11	<-30	35	28	15000	Non-stretched
Comparative example 10	25	PET/I(10)	None	None	0	EM3	11	<-30	35	28	120000	Non-stretched
Comparative example 11	25	PET/I(10)	None	None	0	EM1	21	<-30	15	14	40	Non-stretched
Comparative example 12	25	PET/I(10)	None	None	0	EM7	1	<-30	15	3	20	Non-stretched
Comparative example 13	25	PET/I(10)	None	None	0	EPR	0	<-30	15	1	5	Non-stretched
Comparative example 14	25	PET/I(10)	None	None	0	EM5	7	<-30	15	Not dispersed in fine grains	Not dispersed in fine grains	Non-stretched

*1) Pigment content means weight percentage (wt%) of pigment with respect to total film amount of entire resin and pigment. *2) Silicone of lubricant is added by 3 weight part to 100 weight part of mixed resin. *3) Tetrakis-[methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane of free radical inhibitor is added by 0.1 weight part to 100 weight part of mixed resin. *4) Bond First 20B (manufactured by Sumitomo Chemical Co., Ltd.) of compatibilizing agent is added by 3 weight part to 100 weight part of mixed resin.

[0094]

[Table 3]

Laminated metal sheet	Sample film	Melting point of polyester resin (℃)	Laminating temp. (℃)	Plane orientation coefficient	Thin-wall deep drawn can: Formability	Thin-wall deep drawn can: Impact resistance (room temp.)	Thin-wall deep drawn can: Impact resistance (low temp.)	Thin-wall deep drawn can: Adhesion after forming	Thin-wall deep drawn can: Adhesion after heating	Drawn and ironed can (DI can): Form-ability	Drawn and ironed can (DI can): Impact resistance (room temp.)	Drawn and ironed can (DI can): Impact resistance (low temp.)	Drawn and ironed can (DI can): Adhesion after forming	Drawn and ironed can (DI can): Adhesion after heating
Invention example 35	Invention example 1	215	200	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	○
Invention example 36	Invention example 2	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 37	Invention example 3	255	230	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 38	Invention example 4	250	225	0	◎	◎	◎◎	◎	◎	○	◎	◎◎	○	○
Invention example 39	Invention example 5	255	230	0	◎	◎	◎◎	◎	◎	○	◎	◎◎	○	○
Invention example 40	Invention example 6	230	210	0	◎	◎	◎◎	◎	◎	◎	○	○	◎	◎
Invention example 41	Invention example 7	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 42	Invention example 8	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 43	Invention example 9	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 44	Invention example 10	230	210	0	◎	◎	◎◎	◎	◎	◎	○	○	◎	◎
Invention example 45	Invention example 11	230	210	0	◎	◎	◎◎	◎	◎	○	○	○	○	◎
Invention example 46	Invention example 12	230	210	0	◎	◎	◎◎	◎	◎	◎	○	◎	◎	◎
Invention example 47	Invention example 13	230	210	0	◎	◎	◎◎	◎	◎	◎	○	◎	◎	◎
Invention example 48	Invention example 14	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 49	Invention example 15	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 50	Invention example 16	230	210	0	◎	◎	◎◎	◎	◎	◎	○	◎	◎	◎
Invention example 51	Invention example 17	230	210	0	◎	◎	◎◎	◎	◎	◎	○	○	◎	◎
Invention example 52	Invention example 18	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 53	Invention example 19	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 54	Invention example 20	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 55	Invention example 21	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 56	Invention example 22	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 57	Invention example 23	230	210	0	◎	◎	◎◎	◎	◎	○	◎	◎◎	○	◎
Invention example 58	Invention example 24	230	210	0	◎	◎	◎◎	◎	◎	○	◎	◎	◎	◎

[0095]

[Table 4]

Laminated metal sheet	Sample film	Melting point of polyester resin (℃)	Laminating temp. (℃)	Plane orientation coefficient	Thin-wall deep drawn can					Drawn and ironed can (DI can)				
					Formability	Impact resistance (room temp.)	Impact resistance (low temp.)	Adhesion after forming	Adhesion after heating	Form-ability	Impact resistance (room temp.)	Impact resistance (low temp.)	Adhesion after forming	Adhesion after heating
Invention example 59	Invention example 25	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 60	Invention example 26	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 61	Invention example 27	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 62	Invention example 28	230	210	0	◎	◎	◎◎	◎	◎	○	◎	◎	◎	◎
Invention example 63	Invention example 29	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 64	Invention example 30	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 65	Invention example 31	230	210	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎◎	◎	◎
Invention example 66	Invention example 32	230	210	0.005	◎	◎	◎◎	◎	◎	◎	◎	◎◎◎	◎	◎
Invention example 67	Invention example 33	255	230	0	◎	◎	◎◎	◎	◎	○	◎	◎◎	◎	◎
Invention example 68	Invention example 34	255	230	0	◎	◎	◎◎	◎	◎	○	◎	◎◎	◎	○
Invention example 69	Invention example 2	230	255	0	◎	◎	◎◎	◎	◎	○	◎	◎◎	◎	◎
Invention example 70	Invention example 2	230	230	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 71	Invention example 2	230	190	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 72	Invention example 2	230	170	0	◎	◎	◎◎	◎	◎	◎	◎	◎◎	○	○
Invention example 73	Invention example 32	230	200	0.015	◎	◎	◎◎	◎	◎	○	◎	◎◎◎	◎	◎
Comparative example 15	Comparative example 1	215	200	0	◎	◎	◎◎	◎	◎	△	××	△	△	△
Comparative example 16	Comparative example 2	230	210	0	◎	◎	◎◎	◎	◎	△	××	△	△	○
Comparative example 17	Comparative example 3	255	225	0	◎	◎	◎◎	◎	◎	×	××	△	△	○
Comparative example 18	Comparative example 4	250	230	0	◎	◎	◎◎	◎	◎	△	××	△	△	○
Comparative example 19	Comparative example 5	255	210	0	◎	◎	◎◎	◎	◎	×	××	△	×	○
Comparative example 20	Comparative example 6	230	210	0	◎	◎	◎◎	◎	◎	××	××	△	××	△
Comparative example 21	Comparative example 7	230	210	0	◎	◎	◎◎	◎	◎	○	××	△	△	○
Comparative example 22	Comparative example 8	230	210	0	◎	◎	◎◎	◎	◎	○	×	△	○	◎
Comparative example 23	Comparative example 9	230	210	0	◎	◎	◎◎	◎	◎	×	○	△	×	○
Comparative example 24	Comparative example 10	230	210	0	◎	◎	◎◎	◎	◎	××	○	△	××	○
Comparative example 25	Comparative example 11	230	210	0	◎	◎	◎◎	◎	◎	×	○	△	○	○
Comparative example 26	Comparative example 12	230	210	0	◎	◎	◎◎	◎	◎	△	×	△	○	△
Comparative example 27	Comparative example 13	230	210	0	◎	◎	◎◎	◎	◎	×	××	△	×	×
Comparative example 28	Comparative example 14	230	210	0	◎	◎	◎◎	◎	◎	××	××	△	××	△
Comparative example 29	Invention example 2	230	265	-	-	-	-	-	-	-	-	-	-	-
Comparative example 30	Invention example 2	230	150	-	-	-	-	-	-	-	-	-	-	-

[0096] From Tables 1 to 4, the following facts are found for all can types.

Invention examples 1 to 5 are the films in which a modified polyolefin resin specified in the present invention is dispersed in a polyester resin in which the copolymerization ratio of ethylene terephthalate and ethylene isophthalate is changed variously, and Invention examples 35 to 39 in which the films are laminated under the laminating conditions of the present invention exhibit high formability, impact resistance, and adhesion. Also, Invention example 38 in which the film of Invention example 4 using a polyester resin containing a small amount of isophthalic acid is laminated and Invention example 39 in which the film of Invention example 5 using a homopolyethylene terephthalate is laminated have a tendency toward deteriorated formability and adhesion, but provide high performance as a whole. Also, Invention example 35 in which the film of Invention example 1 using a polyester resin containing a large amount of isophthalic acid is laminated has a tendency toward deteriorated adhesion after heating because of a slightly low melting point, but provides high performance as a whole. Furthermore, Invention examples 33 and 34 are films in which polyester resins with different copolymerization ratios of two types are mixed in the range of the present invention, and Invention examples 67 and 68 in which the films are laminated under the laminating conditions of the present invention have a tendency toward slightly deteriorated formability, but exhibit high formability, impact resistance, and adhesion. On the other hand, Comparative examples 1 to 6 are examples of films in which polyolefin resin is not contained in the polyester resin in which the copolymerization ratio of ethylene terephthalate and ethylene isophthalate is changed variously. Comparative examples 15 to 20 in which these films are laminated especially have a low level of impact

resistance.

[0097]

Invention examples 6 to 10 are mixed resins in which various polyolefin resins are dispersed in the polyester resin, and Invention examples 40 to 44 in which the mixed resins are laminated exhibit high formability, impact resistance, and adhesion. However, Invention example 40 in which the film of Invention example 6 using a polyolefin resin with a slightly high percentage of functional group derived from carboxylic acid is laminated and Invention example 44 in which the film of Invention example 10 using a polyolefin resin having a slightly high glass-transition temperature is laminated have a tendency toward slightly deteriorated low-temperature impact resistance. On the other hand, Comparative examples 11 to 13 are mixed resins in which a polyolefin resin containing a functional group derived from carboxylic acid whose percentage deviates from the range of the present invention is dispersed in the polyester resin, and Comparative examples 25 to 27 in which these mixed resins are laminated have inferior formability and impact resistance.

[0098]

Comparative example 14 is a film in which a modified polyolefin resin with a group derived from carboxylic acid and a polyester resin are simply mixed with each other, and Comparative example 28 in which this film is laminated has greatly deteriorated formability and impact resistance because the modified polyolefin resin is not dispersed in the polyester resin in a fine granular form.

[0099]

Invention examples 11 to 18 are films in which the blending ratio and dispersion state of the modified polyolefin resin in the polyester resin are changed variously in the range of the present invention, and Invention examples 45 to 52 in which the films are

laminated under the laminating conditions of the present invention exhibit high formability, impact resistance, and adhesion. However, Invention example 45 in which the film of Invention example 11 containing a small amount of dispersed modified polyolefin resin is laminated and Invention example 51 in which the film of Invention example 17 having a very large number of grains of the modified polyolefin resin is laminated have a tendency toward slightly deteriorated low-temperature impact resistance.

[0100]

On the other hand, Comparative examples 7 to 10 are films in which the blending ratio of modified polyolefin resin in the polyester resin does not meet the requirement of the present invention, and Comparative examples 21 to 24 in which the films are laminated under the laminating conditions of the present invention have greatly deteriorated formability and impact resistance. Comparative examples 21 and 22 in which the films of Comparative examples 7 and 8 containing a small amount of dispersed modified polyolefin resin are laminated have greatly deteriorated room-temperature impact resistance, and Comparative examples 23 and 24 in which the films of Comparative examples 9 and 10 containing a large amount of modified polyolefin resin are laminated have greatly deteriorated formability.

[0101]

Invention examples 19 to 23 are films in which a titanium dioxide pigment is mixed with a mixed resin of modified polyolefin resin and polyester resin, and Invention examples 53 to 57 in which the films are laminated under the laminating conditions of the present invention exhibit high formability, impact resistance, and adhesion, and also provide a white uniform color tone. However, Invention example 53 in which the film of Invention example 19 in which the added amount of pigment is smaller than the desired range is laminated has

slightly insufficient opacifying property of color tone. On the other hand, Invention example 57 in which the film of Invention example 23 in which the added amount of pigment is larger than a desired range is laminated has slightly deteriorated formability.

[0102]

Invention examples 24 to 28 are films in which the thickness thereof is changed in the range of the present invention, and Invention examples 58 to 62 in which the films are laminated under the laminating conditions of the present invention exhibit high formability, impact resistance, and adhesion. Invention examples 24 and 28 are films in which the thickness thereof exceeds the desired range of the present invention, and Invention examples 58 and 62 in which the films are laminated have slightly lower formability and impact resistance than the case of desired film thickness.

[0103]

Invention examples 36 and 69 to 72 are films obtained by changing the laminating conditions of the film of Invention example 2 in the range of the present invention. If the conditions are within the range of the present invention, high formability, impact resistance, and adhesion are exhibited regardless of the laminating temperature. On the other hand, in Comparative example 30, the film of Invention example 2 was laminated under conditions lower than the lower limit of laminating temperature range of the present invention, thus the film did not adhere to a steel sheet, and therefore evaluation could not be made. On the other hand, in Comparative example 29, the film of Invention example 2 was laminated under conditions exceeding the upper limit of laminating temperature range of the present invention, thus the film fused to a laminate roll, and therefore evaluation could not be made.

[0104]

Invention examples 29 to 31 are films in which a lubricant, a free radical inhibitor, and a compatibilizing agent are mixed, respectively, in a mixed resin of modified polyolefin resin and polyester resin of the present invention, and Invention examples 63 to 65 in which the films are laminated under the laminating conditions of the present invention exhibit high formability, impact resistance, and adhesion. Furthermore, Invention examples 63 to 65 also have lubricity, free radical deterioration resistance, and compatibility depending on the function of added additive, and in particular, Invention example 65 exhibits excellent low-temperature impact resistance.

[0105]

Invention example 32 is a film of the present invention that is manufactured by the two-axis stretching method, and Invention examples 66 and 73 in which the film is laminated exhibit high performance. Invention example 73, which has a plane orientation coefficient of 0.015, exhibits a slightly deteriorated formability. However, in the low-temperature impact resistance test, it was verified that the formability is slightly higher than the case of low plane orientation coefficient. Invention example 66, which has a plane orientation coefficient in the range of the present invention, exhibits very high formability and impact resistance.

[0106]

<Example 2>

A modified polyolefin resin with a group derived from carboxylic acid having a primary grain diameter of 0.3 μm, which was a starting raw material, was cold-blended with a polyester resin in a blending ratio given in Tables 5 and 6 using a tumbler blender, and then the blended resin was melted and kneaded at 260℃ using a twin screw extruding machine, by which a raw material pellet of polyester

resin in which the modified polyolefin resin was dispersed was obtained.

[0107]

As a metal sheet, as in Example 1, a tin-free steel (hereinafter abbreviated to TFS) with a thickness of 0.18 mm for thin-wall deep drawn can and 0.23 mm for DI can, which had a degree of temper of DR9, metallic chromium layer of 80 mg/m^2, and chromium oxide layer of 15 mg/m^2 (metallic chromium conversion), was used, by which a both-side resin laminated metal sheet was obtained by a method in which the raw material resin pellet was charged to a single screw extruding machine, molten resin was extruded directly from a T-die onto one surface of the metal sheet, the extruded resin was once cooled while being held adherently between two rolls, and immediately after the resin was laminated on the opposite surface in the same manner, the resin laminated metal sheet was cooled rapidly in water. The temperature of metal sheet at the laminating time was 50℃. The lip opening width of T-die was adjusted so that the thickness of resin film was in a range from 6 to 55 μm. The type of sample resin and the resin melting temperature during laminating are given in Tables 7 and 8. The used polyester resin and modified polyolefin resin with a group derived from carboxylic acid are the same as those used in Example 1.

[0108]

A pelletized modified polyolefin resin with a group derived from carboxylic acid, which was a starting raw material, was mixed with the polyester resin in a blending ratio given in Comparative example 43 in Table 6, the mixed resin was melted and kneaded at 260℃ using a single screw extruding machine, and the obtained mixed resin of modified polyolefin resin and polyester resin was extruded from a T-die, by which the resin that had been directly extruded to a thickness of 25 μm was laminated to the TFS.

[0109]

All of the grain diameter of modified polyolefin resin dispersed in resin film, various temperatures in the table, and the method for measuring the plane orientation coefficient of laminated metal sheet are the same as those in Example 1. As in Example 1, a thin-wall deep drawn can or a DI can was manufactured from the laminated metal sheet obtained as described above, and the can was subjected to straightening heat treatment to manufacture a sample can. The formability, impact resistance, and adhesion of film of the manufactured can body were investigated as in Example 1. The investigation results are given in Tables 7 and 8.

[0110]

[Table 5]

Laminated metal sheet	Polyester resin		Pigment		Polyolefin resin					
	Resin type	Additive	Kind	Content *1)	Resin type	Weight percentage of functional group derived from carboxylic acid (wt%)	Tg (℃)	Blending ratio in entire resin (wt%)	Volume percentage of grains with diameter of 0.1 to 5 μm (vol%)	Number of grains with diameter of 0.1 to 5 μm in cube with one side of 10 μm (grains)
Invention example 74	PET/I(18)	None	None	0	EM4	8	<-30	15	14	2500
Invention example 75	PET/I(10)	None	None	0	EM4	8	<-30	15	14	2500
Invention example 76	PET/I(10)	None	None	0	EM4	8	<-30	15	14	2500
Invention example 77	PET/I(10)	None	None	0	EM4	8	<-30	15	14	2500
Invention example 78	PET/I(10)	None	None	0	EM4	8	<-30	15	14	2500
Invention example 79	PET/I(10)	None	None	0	EM4	8	<-30	15	14	2500
Invention example 80	PET/I(5)	None	None	0	EM4	8	<-30	15	14	2500
Invention example 81	PET/I(2)	None	None	0	EM4	8	<-30	15	14	2500
Invention example 82	PET	None	None	0	EM4	8	<-30	15	14	2500
Invention example 83	PET/I(10)	None	None	0	EM2	18	<-30	15	15	1000
Invention example 84	PET/I(10)	None	None	0	EM4	8	<-30	15	14	2500
Invention example 85	PET/I(10)	None	None	0	EM5	7	<-30	15	14	2500
Invention example 86	PET/I(10)	None	None	0	EM6	5	<-30	15	14	2500
Invention example 87	PET/I(10)	None	None	0	EM8	6	20	15	14	2500
Invention example 88	PET/I(10)	None	None	0	EM3	11	<-30	5	4	4
Invention example 89	PET/I(10)	None	None	0	EM3	11	<-30	5	8	100
Invention example 90	PET/I(10)	None	None	0	EM3	11	<-30	10	10	50
Invention example 91	PET/I(10)	None	None	0	EM3	11	<-30	10	12	500
Invention example 92	PET/I(10)	None	None	0	EM3	11	<-30	15	18	800
Invention example 93	PET/I(10)	None	None	0	EM3	11	<-30	15	20	22000
Invention example 94	PET/I(10)	None	None	0	EM3	11	<-30	20	24	250000
Invention example 95	PET/I(10)	None	None	0	EM3	11	<-30	25	22	10000
Invention example 96	PET/I(10)	None	TiO_2	3	EM5	7	<-30	15	14	2500
Invention example 97	PET/I(10)	None	TiO_2	7	EM5	7	<-30	15	14	2500
Invention example 98	PET/I(10)	None	TiO_2	15	EM5	7	<-30	15	14	2500
Invention example 99	PET/I(10)	None	TiO_2	30	EM5	7	<-30	15	14	2500
Invention example 100	PET/I(10)	None	TiO_2	50	EM5	7	<-30	15	14	2500

*1) Pigment content means weight percentage (wt%) of pigment with respect to total film amount of entire resin and pigment.

[0111]

[Table 6]

Laminated metal sheet	Polyester resin		Pigment		Polyolefin resin					
	Resin type	Additive	Kind	Content *1)	Resin type	Weight percentage of functional group derived from carboxylic acid (wt%)	Tg (℃)	Blending ratio in entire resin (wt%)	Volume percentage of grains with diameter of 0.1 to 5 μm (vol%)	Number of grains with diameter of 0.1 to 5 μm in cube with one side of 10 μm (grains)
Invention example 101	PET/I(10)	None	None	0	EM6	5	<-30	15	14	2500
Invention example 102	PET/I(10)	None	None	0	EM6	5	<-30	15	14	2500
Invention example 103	PET/I(10)	None	None	0	EM6	5	<-30	15	14	2500
Invention example 104	PET/I(10)	None	None	0	EM6	5	<-30	15	14	2500
Invention example 105	PET/I(10)	None	None	0	EM6	5	<-30	15	14	2500
Invention example 106	PET/I(10)	*2)0.3wt%	None	0	EM3	11	<-30	15	14	2500
Invention example 107	PET/I(10)	*3)0.1wt%	None	0	EM3	11	<-30	15	14	2500
Invention example 108	PET/I(10)	*4)3wt%	None	0	EM3	11	<-30	15	14	2500
Invention example 109	PET70%+ PET/I(10)30%	None	None	0	EM4	8	<-30	15	14	2500
Invention example 110	PET40%+ PET/I(18)60%	None	None	0	EM4	8	<-30	15	14	2500
Comparative example 31	PET/I(18)	None	None	0	None	-	-	0	0	0
Comparative example 32	PET/I(10)	None	None	0	None	-	-	0	0	0
Comparative example 33	PET/I(5)	None	None	0	None	-	-	0	0	0
Comparative example 34	PET/I(2)	None	None	0	None	-	-	0	0	0
Comparative example 35	PET	None	None	0	None	-	-	0	0	0
Comparative example 36	PET/I(10)	None	None	0	EM3	11	<-30	2	3	5
Comparative example 37	PET/I(10)	None	None	0	EM3	11	<-30	2	3	50
Comparative example 38	PET/I(10)	None	None	0	EM3	11	<-30	35	30	20000
Comparative example 39	PET/I(10)	None	None	0	EM3	11	<-30	35	30	130000
Comparative example 40	PET/I(10)	None	None	0	EM1	21	<-30	15	16	50
Comparative example 41	PET/I(10)	None	None	0	EM7	1	<-30	15	4	40
Comparative example 42	PET/I(10)	None	None	0	EPR	0	<-30	15	1	4
Comparative example 43	PET/I(10)	None	TiO_2	3	EM5	7	<-30	15	Not dispersed in fine grains	Not dispersed in fine grains

*1) Pigment content means weight percentage (wt%) of pigment with respect to total film amount of entire resin and pigment.
*2) Silicone of lubricant is added by 3 weight part to 100 weight part of mixed resin.
*3) Tetrakis-[methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane of free radical inhibitor is added by 0.1 weight part to 100 weight part of mixed resin.
*4) Bond First 20B (manufactured by Sumitomo Chemical Co., Ltd.) of compatibilizing agent is added by 3 weight part to 100 weight part of mixed resin.

[0112]

[Table 7]

Laminated metal sheet	Melting point of mixed resin (melting point of polyester resin) (℃)	Melting temp. of mixed resin (℃)	Resin thickness (μm)	Thin-wall deep drawn can					Drawn and ironed can (DI can)				
				Formability	Impact resistance (room temp.)	Impact resistance (low temp.)	Adhesion after forming	Adhesion after heating	Formability	Impact resistance (room temp.)	Impact resistance (low temp.)	Adhesion after forming	Adhesion after heating
Invention example 74	215	235	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	○
Invention example 75	230	235	25	◎	◎	◎◎	◎	◎	○	◎	◎	○	◎
Invention example 76	230	240	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 77	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 78	230	265	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 79	230	275	25	◎	◎	◎◎	◎	◎	○	○	○	○	◎
Invention example 80	255	275	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 81	250	270	25	◎	◎	◎◎	◎	◎	○	◎	◎◎	○	○
Invention example 82	255	275	25	◎	◎	◎◎	◎	◎	○	◎	◎◎	○	○
Invention example 83	230	250	25	◎	◎	◎◎	◎	◎	◎	○	○	◎	◎
Invention example 84	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 85	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 86	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 87	230	250	25	◎	◎	◎◎	◎	◎	◎	○	○	◎	◎
Invention example 88	230	250	25	◎	◎	◎◎	◎	◎	○	○	○	○	◎
Invention example 89	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎	◎	◎
Invention example 90	230	250	25	◎	◎	◎◎	◎	◎	◎	○	◎	◎	◎
Invention example 91	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 92	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 93	230	250	25	◎	◎	◎◎	◎	◎	◎	○	◎	◎	◎
Invention example 94	230	250	25	◎	◎	◎◎	◎	◎	◎	○	○	◎	◎
Invention example 95	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 96	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 97	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 98	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 99	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 100	230	250	25	◎	◎	◎◎	◎	◎	○	◎	◎◎	○	◎

*1) Pigment content means weight percentage (wt%) of pigment with respect to total film amount of entire resin and pigment.

[0113]

[Table 8]

Laminated metal sheet	Melting point of mixed resin (melting point of polyester resin) (℃)	Melting temp. of mixed resin (℃)	Resin thickness (μm)	Thin-wall deep drawn can					Drawn and ironed can (DI can)				
				Formability	Impact resistance (room temp.)	Impact resistance (low temp.)	Adhesion after forming	Adhesion after heating	Form-ability	Impact resistance (room temp.)	Impact resistance (low temp.)	Adhesion after forming	Adhesion after heating
Invention example 101	230	250	6	◎	◎	◎◎	◎	◎	○	◎	◎	◎	◎
Invention example 102	230	250	15	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 103	230	250	20	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 104	230	250	40	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 105	230	250	55	◎	◎	◎◎	◎	◎	○	◎	◎	◎	◎
Invention example 106	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 107	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎	◎	◎
Invention example 108	230	250	25	◎	◎	◎◎	◎	◎	◎	◎	◎◎◎	◎	◎
Invention example 109	255	275	25	◎	◎	◎◎	◎	◎	○	◎	◎◎	◎	◎
Invention example 110	255	275	25	◎	◎	◎◎	◎	◎	○	◎	◎◎	◎	○
Comparative example 31	230	250	25	◎	◎	◎◎	◎	◎	△	××	△	△	△
Comparative example 32	255	275	25	◎	◎	◎◎	◎	◎	△	××	△	△	○
Comparative example 33	250	270	25	◎	◎	◎◎	◎	◎	△	××	△	△	○
Comparative example 34	255	275	25	◎	◎	◎◎	◎	◎	×	××	△	×	○
Comparative example 35	230	250	25	◎	◎	◎◎	◎	◎	××	××	△	××	△
Comparative example 36	230	250	25	◎	◎	◎◎	◎	◎	○	××	△	△	○
Comparative example 37	230	250	25	◎	◎	◎◎	◎	◎	○	×	△	○	◎
Comparative example 38	230	250	25	◎	◎	◎◎	◎	◎	×	△	△	×	○
Comparative example 39	230	250	25	◎	◎	◎◎	◎	◎	××	△	△	××	○
Comparative example 40	230	250	25	◎	◎	◎◎	◎	◎	×	△	△	○	○
Comparative example 41	230	250	25	◎	◎	◎◎	◎	◎	△	×	△	○	△
Comparative example 42	230	250	25	◎	◎	◎◎	◎	◎	×	××	△	×	×
Comparative example 43	230	250	25	◎	◎	◎◎	◎	◎	××	××	△	××	△

*1) Pigment content means weight percentage (wt%) of pigment with respect to total film amount of entire resin and pigment.
*2) Silicone of lubricant is added by 3 weight part to 100 weight part of mixed resin.
*3) Tetrakis-[methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane of free radical inhibitor is added by 0.1 weight part to 100 weight part of mixed resin.
*4) Bond First 20B (manufactured by Sumitomo Chemical Co., Ltd.) of compatibilizing agent is added by 3 weight part to 100 weight part of mixed resin.

[0114]

From Tables 5 to 8, the following facts are found for either can type. Invention examples 74 to 82 are films which are formed by dispersing a modified polyolefin resin specified in the present invention in a polyester resin in which the copolymerization ratio of ethylene terephthalate and ethylene isophthalate is changed variously, and exhibit high formability, impact resistance, and adhesion. Also, Invention example 81 using a polyester resin containing a small amount of isophthalic acid and Invention example 82 using a homopolyethylene terephthalate have a tendency toward deteriorated formability and adhesion, but provide high performance as a whole. Also, Invention example 74 using a polyester resin containing a large amount of isophthalic acid has a tendency toward deteriorated adhesion after heating because of slightly low melting point, but provides high performance as a whole. Furthermore, Invention examples 109 and 110 are resins in which polyester resins with different copolymerization ratio of two types are mixed in the range of the present invention, and have a tendency toward slightly deteriorated formability, but exhibit high formability, impact resistance, and adhesion. On the other hand, Comparative examples 31 to 35 are examples of resins in which polyolefin resin is not contained in the polyester resin in which the copolymerization ratio of ethylene terephthalate and ethylene isophthalate is changed variously, and especially have a low level of impact resistance.

[0115]

Invention examples 83 to 87 are examples of mixed resins in which various polyolefin resins are dispersed in the polyester resin, and exhibit high formability, impact resistance, and adhesion. However, Invention example 83 using a polyolefin resin with a slightly high percentage of functional group derived from carboxylic acid and

Invention example 87 using a polyolefin resin with a slightly high glass-transition temperature have a tendency toward slightly deteriorated low-temperature impact resistance. On the other hand, Comparative examples 40 to 42 are mixed resins in which a polyolefin resin containing a functional group derived from carboxylic acid whose percentage deviates from the range of the present invention is dispersed in the polyester resin, and have inferior formability and impact resistance.

[0116]

Comparative example 43 is a resin in which a modified polyolefin resin with a group derived from carboxylic acid and a polyester resin are simply mixed with each other, and has greatly deteriorated formability and impact resistance because the modified polyolefin resin is not dispersed in the polyester resin in a fine granular form.

[0117]

Invention examples 88 to 95 are resins in which the blending ratio and dispersion state of the modified polyolefin resin in the polyester resin are changed variously in the range of the present invention, and exhibit high formability, impact resistance, and adhesion. However, the resin of Invention example 88 containing a small amount of dispersed modified polyolefin resin and the resin of Invention example 94 having a very large number of grains of modified polyolefin resin have a tendency toward slightly deteriorated low-temperature impact resistance.

[0118]

On the other hand, Comparative examples 36 to 39 are resins in which the blending ratio of modified polyolefin resin in the polyester resin does not meet requirement of the present invention, and have greatly deteriorated formability and impact resistance.

Comparative examples 36 and 37 containing a small amount of dispersed modified polyolefin resin have greatly deteriorated room-temperature impact resistance, and Comparative examples 38 and 39 containing a large amount of modified polyolefin resin have greatly deteriorated formability.

[0119]

Invention examples 96 to 100 are resins in which a titanium dioxide pigment is mixed with a mixed resin of modified polyolefin resin and polyester resin, and exhibit high formability, impact resistance, and adhesion, and also provide a white uniform color tone. However, Invention example 96 in which the added amount of pigment is smaller than a desired range has slightly insufficient opacifying property of color tone. On the other hand, Invention example 100 in which the added amount of pigment is larger than a desired range has slightly deteriorated formability.

[0120]

Invention examples 101 to 105 are resins in which the thickness thereof is changed in the range of the present invention, and exhibit high formability, impact resistance, and adhesion. Invention examples 101 and 105 are resins in which the thickness thereof exceeds the desired range of the present invention, and have slightly lower formability and impact resistance than the case of desired film thickness.

[0121]

Invention examples 75 to 79 are resins obtained by changing the extrusion laminating conditions in the range of the present invention. If the conditions are within the range of the present invention, high formability, impact resistance, and adhesion are exhibited regardless of the laminating temperature. Invention example 75 was laminated under conditions lower than the desired lower

limit of laminating temperature range, and Invention example 79 was laminated under conditions exceeding the desired upper limit of laminating temperature range, thus these Invention examples have slightly deteriorated formability and low-temperature impact resistance.

[0122]

Invention examples 106 to 108 are resins in which a lubricant, a free radical inhibitor, and a compatibilizing agent are mixed, respectively, in a mixed resin of modified polyolefin resin and polyester resin of the present invention, and exhibit high formability, impact resistance, and adhesion. Furthermore, Invention examples 106 to 108 also have lubricity, free radical deterioration resistance, and compatibility depending on the function of added additive, and in particular, Invention example 108 exhibits excellent low-temperature impact resistance.

[0123]

[Effect of the Invention]

The present invention provides a resin film for metal sheet laminate having excellent formability, impact resistance, and adhesion, and provides a laminated metal sheet, and a method for manufacturing the same. The laminated metal sheet according to the present invention is suitably used for a two-piece metallic can manufactured by drawing or ironing, and also for a lid portion of two-piece can or a sidewall, a lid, and a bottom of three-piece can. The laminated metal sheet according to the present invention is also suitable as a material for a thin-wall deep drawn can which is subjected to particularly severe forming in a current state of thinning the can wall thickness by reducing sheet thickness of the material.

[Designation of Document] ABSTRACT

[Abstract]

[Problem] The object is to provide a resin film for metal sheet laminate which endures severe forming owing to excellent formability and impact resistance, and also to excellent adhesion after forming and heating, further gives stable performance independent of forming conditions, and also provides a laminated metal sheet, and a method for manufacturing the same.

[Means for Resolution] The resin film for metal sheet laminate has a mixed resin in which a granular resin mainly existing in a state of grains having 0.1 to 5 μm in diameter is dispersed in a polyester resin having a main basic skeleton of polyethylene terephthalate and/or isophthalic acid copolymerized polyethylene terephthalate, in a range from 3 to 30% by weight in entire resin. The granular resin is a modified polyolefin resin containing a functional group derived from carboxylic acid in a range from 2 to 20% by weight as carboxylic acid.

[Selected Drawing] None